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D.M. Neumark
(Ph.D. Thesis)

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HIGH RESOLUTION REACTIVE SCATTERING

Daniel M. Neumark
(Ph.D. Thesis)

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Berkeley, California 94720

This work was supported by the Assistant Secretary for Energy Research,
Office of Basic Energy Sciences, Chemical Sciences Division of the
U.S. Department of Energy under Contract No. DE-AC03-76SF00098
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Abstract

A high resolution reactive scattering study has been performed on the reactions

\[ F + H_2 \rightarrow HF + H \]
\[ F + D_2 \rightarrow DF + D \]
\[ F + HD \rightarrow HF + D \]
\[ F + HD \rightarrow DF + H \]

using the crossed molecular beams technique. The resolution of the apparatus was sufficient to allow the determination of differential cross sections and kinetic energy distributions for each HF(DF) vibrational state. This level of detail was necessary to ascertain the role of dynamical resonances in these reactions.

Chapter I presents a detailed investigation of the \( F + n-H_2 \) and \( F + \text{para-}H_2 \) reactions at several collision energies. The primary result is the observation of considerable forward scattering for the HF\( (v = 3) \) product over the entire energy range whereas the \( v = 2 \) and \( v = 1 \) states are predominantly backward-scattered. This leads to the conclusion that the production of HF \( (v = 3) \) is strongly influenced by resonance effects, in contrast to the results of quantal reactive scattering calculations which predict these effects to appear in the
\( v = 2 \) channel. This discrepancy is attributed to inadequacies in the potential energy surface used in the calculations, and the experimental results indicate several ways in which the surface should be modified.

The major focus of Chapter II is the effect of isotopic substitution on the product angular distributions. The strength of dynamical resonance effects has been predicted to vary considerably for the four reactions under study. The results in this chapter on the \( F + D_2 \) and \( F + HD \) reactions show dramatic differences in the product angular distributions well beyond what is expected based on classical trajectory calculations, but which are consistent with the predicted dependence of resonance effects on isotopic substitution. This supports the interpretation of the \( F + H_2 \) results in Chapter I in terms of dynamical resonances.

The results presented here represent the first definitive observation of dynamical resonance effects in reactive scattering. This is, in principle, equivalent to performing vibrational spectroscopy on the transition state, and therefore provides a highly sensitive probe of the region of the potential energy surface which governs the important properties of a chemical reactions.
Acknowledgments

The research described in this thesis marks the culmination (a dangerous word in the Lee group) of a project begun in the late 1960's. By this standard, my own seemingly endless sojourn at Berkeley is not so long, after all. The point is that many people have invested a lot of time on this project, and, although only the results obtained within the last year are discussed here, these could not have been obtained without the groundwork prepared by others.

Professor Yuan Lee provided the driving force behind this project. He not only came up with many of the ideas for apparatus modifications in order to improve the experiment, but he also formulated the critical connection between our experiment and the theoretical calculations which was the basis for interpreting our results. Yuan insisted on pushing on with the project whereas many would have faltered, and I hope some of his perseverance has rubbed off on me during my stay at Berkeley.

My collaborators on the work described here were Alec Wodtke and Gary Robinson. I found working with both of them to be stimulating and challenging. Alec designed the fluorine source used in the experiments, and Gary filled an increasingly invaluable role in running the machine when my energies turned more towards data analysis. Mike Valentine was hired by Yuan to synthesize HD in the mass quantities needed for the experiment when it became clear that nobody else would do it.
In the earlier phases of this project, I worked closely with Carl Hayden who, among other things, designed a lot of the electronics still in use on the apparatus. His competence is evident from the fact that none of his creations have malfunctioned even though he graduated from the Lee group almost two years ago. This is indeed fortunate, as his record-keeping was not nearly as good as his design-work. I still can’t find the circuit diagrams for most of his fabrications. I also worked with Randy Sparks and Dr. Kosuke Shobatake on this project during my first year at Berkeley. Randy built the apparatus on which these experiments were performed, and Kosuke took care of many of the myriad details needed to make a molecular beam machine functional. Kosuke also wrote most of the computer program used in the data analysis.

During the course of this work, I have discussed the results with several theoreticians who have provided valuable insight into their interpretation. I particularly wish to thank Professor Robert Wyatt, Dr. Bob Walker, Dr. Eli Pollak, and Dr. James Muckerman for their help in this regard.

I have had the pleasure of working and dealing with most of the members of the Lee group over the years, and especially thank Tim Minton for his collaboration on work still in progress but which should soon see the light of day. I have benefited considerably from the advice (solicited and otherwise) of Matt Vernon and Dr. Jeremy Frey. Ann Weightman was invaluable in the last desperate days of my
graduate career for steering me through the University bureaucracy, and for ensuring that the group word processor was always in good working order. I would also like to thank the people who provided a high level of technical support for the projects I worked on, especially Charlie Taylor, Fred Wolff and his gang, Jim Peck, Ed Voronin, Don Wilkinson, Fred Vogelsberg, and Ed Arnold. My high school chemistry teacher, Mr. Frank Cardulla, deserves special mention for initially sparking my interest in chemistry.

Finally, I reserve very special thanks for my fiancee and overall favorite human being, Ellen Kalmuk, who will be my wife within a week of writing this Acknowledgment. I don't think I could have survived graduate school without her love and support over the years.

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CHAPTER I
Molecular Beam Studies of the F + H₂ reaction

Introduction

The reaction, F + H₂ → HF + H, has been extensively studied over the past 15 years. Although much of the early interest in this reaction centered on its application to chemical lasers, it has become a prototype in the field of reaction dynamics because of its accessibility to both detailed theoretical and experimental study. It was one of the first reactions in which vibrationally state-resolved product distributions were measured; chemical laser¹ and infrared chemiluminescence studies²a,²b at thermal energies showed that the HF vibrational distribution was highly inverted with most of the population in v = 2 and v = 3. The effect of varying reactant translation and rotation on the final state distributions was later investigated using the same techniques.³⁻⁷ The F + D₂ reaction was the first reaction in which vibrationally state-resolved product angular distributions were obtained in a crossed molecular beams experiment.⁸ The results showed that all the products were predominantly backward-scattered, indicating that collinear approach of the reactants is most likely to lead to reaction. Accurate rate constants for F + H₂ and F + D₂ have recently been determined over a wide temperature range using various experimental methods.⁹,¹⁰

Theoretical studies have been concerned with developing an accurate potential energy surface for the reaction as well as formulating techniques for scattering calculations to be performed on model surfaces in order to gain additional insight into the reaction dynamics.
of this system. An ab initio potential energy surface has been calculated and has provided important information on the general features of the true surface, but as its exothermicity and barrier height are incorrect, scattering calculations using it cannot be meaningfully compared to experimental results until the accuracy of the ab initio calculation is further improved. A seemingly more productive approach has been to carry out classical trajectory calculations on model semi-empirical surfaces, usually of the LEPS form, and to optimize the surface parameters in order to match the experimental results. The most extensive studies of this type have been performed by Muckerman, Polanyi, and their coworkers, who investigated the effects of small changes in the surface on the reaction cross section and the product angular distribution. Polanyi's study showed that reactant translational energy had a substantially greater effect on the reaction dynamics than vibrational energy. This is the expected result for an exothermic reaction with a barrier in the entrance channel.

The potential energy surface most commonly used in reactive scattering studies of $\text{F}+\text{H}_2$ is the Muckerman 5 (M5) surface. This is an LEPS surface with the correct exothermicity upon which classical trajectory calculations reproduce the rate constant determined by Mercer et al. and the experimental values for product energy disposal. The surface has a barrier of 1.064 kcal/mole in the entrance channel for collinear approach of the reactants which rises rapidly as the F-H-H bending angle increases. Several problems are found to be associated with this surface, however. Mercer's value for
the activation energy was 1.71 kcal/mole, but more reliable recent studies\textsuperscript{9,10} show that $E_a$ is closer to 1.0 kcal/mole. In addition, the pre-exponential $A$ factor of the rate constant for M5 derived from trajectory studies is considerably lower than the $A$ factor determined in the newer experiments.\textsuperscript{19} The larger activation energy and smaller $A$ factor suggest that the entrance channel barrier on M5 is too high and rises too quickly with increasing deviation from collinear approach. Besides, as was mentioned by Jakubetz and Connor\textsuperscript{20}, the whole approach in which classical trajectory calculations are used to test the ability of a surface to reproduce experimental data may be invalid if quantum effects are important.

Quantum mechanical scattering calculations have indeed predicted that quantal effects in the form of dynamical resonances\textsuperscript{21} should play a significant role in the reaction dynamics of $F + H_2$. A quantal collinear reactive scattering calculation by Schatz et al. of the reaction probability vs. collision energy on the M5 surface is displayed in figure 1.\textsuperscript{22} The $P_{02}$ and $P_{03}$ curves are for the reaction from $H_2 (v = 0)$ to form $HF (v = 0)$ and $v = 3$, respectively. Both curves show broad features due to direct scattering, and the $P_{02}$ curve shows an additional sharp peak with a width of about 0.01 eV. Argand diagrams and time delay analysis show that the sharp $P_{02}$ peak is due to interference between direct and resonant reactive scattering.\textsuperscript{23,24} Calculations at higher energy also display strong resonance effects, with peaks typically occurring near a threshold for an HF vibrational state.\textsuperscript{22,25} Connor has performed collinear calculations on several surfaces and obtained dramatically different resonance structure for
each case.\textsuperscript{25} This indicates that the exact nature of the resonances depends critically on the details of the potential energy surface in the strong coupling region near the transition state. This is the most important region of the surface as it determines many of the experimental observables mentioned previously.

The results of reactive scattering and kinetics experiments are, in general, a reflection of the properties of the transition state and the strong coupling region, but it is difficult to work backwards and determine anything conclusive about the structure of the potential energy surface. Attempts to study the transition state via emission and absorption have not yielded much information as these experiments typically involve electronic transitions between two unknown repulsive surfaces.\textsuperscript{26-28,28a} The experimental observation of resonances should therefore provide a considerably more direct and sensitive probe of the strong coupling region than has previously been available. As this will yield information on quasi-bound states supported by the potential energy surface, the observation of resonances is, in principle, equivalent to performing vibrational spectroscopy of the transition state.\textsuperscript{24} We have performed a high resolution crossed molecular beams study of the F + H\textsubscript{2} reaction in an attempt to observe the effects of dynamical resonances. In order to view our results in the proper perspective, it is necessary to understand what features of the potential energy surface cause resonances to appear in collinear and three-dimensional calculations, and how dynamical resonances can actually be observed in a reactive scattering experiment.
Properties of Dynamical Resonances

The identification of the elements of the potential energy surface responsible for the resonances is not entirely straightforward. The physical origin of reactive resonances has been shown to be the existence of quasi-bound FH₂ states localized in the strong coupling region of the surface which live for a short time before decomposing to products.²⁴,²⁹ It is not immediately clear why these states should exist at all; the M5 surface, for example, has no wells in the strong coupling region which one might think are necessary to support quasi-bound states.

The origin of dynamical resonances can be understood by first considering a collinear scattering calculation. If the scattering wavefunction is separated into translational and vibrational motion, vibrationally adiabatic curves can be derived which are basically effective potentials for the translational motion of reactants or products described by a single quantum number for the vibrational action.³⁰,³¹ Even in the absence of wells on the potential energy surface, the adiabatic curves can develop barriers and wells as the potential energy surface perpendicular to the translational coordinate narrows and widens, respectively, and these features become more pronounced for the curves corresponding to higher vibrational quantum numbers. The wells can support quasi-bound states which behave like shape or Feshbach resonances and provide an additional pathway between reactants and products.
The problem with this picture is that the adiabatic curves are highly coordinate-dependent. In reactive scattering, it is not clear how to unambiguously define translation and vibration in a global manner that describes reactants and products. This is exacerbated in \( F + H_2 \) which is clearly not a vibrationally adiabatic reaction. An important stop towards resolving this dilemma is due to the work of Pollak and coworkers on periodic orbit dividing surfaces (PODS), which are classical stable orbits on a potential energy surface\(^{32} \). They proved that a PODS with vibrational action \((n + 1/2)\hbar\) corresponds to either an adiabatic well or a barrier for the state \( v = n \).\(^{33} \) The PODS is an intrinsic property of the potential energy surface and does not depend on any coordinate system. In fact, each PODS defines a locally adiabatic coordinate system in which vibration is parallel to the bound orbit and translation is perpendicular to it. In addition to locating the adiabatic wells and barriers, Pollak and Child have found another set of PODS which, when subjected to a quantization condition, match very well with the resonance energies in the quantal calculations.\(^{34} \) The orbits for these resonant PODS oscillate between the reactant and product sides of the critical region just inside the adiabatic barriers. The orbit corresponding to the lowest \( F+H_2 \) resonance is bounded by the \( v = 0 \) reactant and \( v = 3 \) product barriers.

The PODS formulation provides an easily visualized picture of dynamical resonances. However, as the PODS corresponding to the resonances are classical bound orbits, they cannot be accessed by reactants or products in a classical calculation. The coupling
between the bound orbits and the continuum can be estimated by incorporating a semi-classical approximation into the theory, but extending this procedure to \( F + H_2 \) is difficult because the resonance has several decay pathways. In order to better understand the results of the quantal reactive scattering calculations, it is desirable to construct a global coordinate system in which the adiabatic curves retain some physical significance even for a non-adiabatic process. The best one can do is to devise a system in which the reaction can be described with as few adiabatic curves as possible. Natural collision coordinates do not work well in this regard for \( F + H_2 \). Far more success has resulted using hyperspherical coordinates.

Figure 2 shows the collinear M5 surface in skewed, mass-weighted coordinates. Region II is the reactant valley and region III is the product valley. The hyperspherical coordinates, \( \rho \) and \( \alpha \), are defined in the figure. The translational coordinate is the hyper-radius \( \rho \), which is a measure of the size of the \( FH_2 \) complex, and the vibrational coordinate is the angle, \( \alpha \), which describes the evolution of the complex from reactants to products.

The adiabatic curves derived by Launay and Le Dourneuf are shown in figure 3. The curves are determined by finding the eigenvalues of the potential energy surface at constant \( \rho \) and adding on two smaller terms: a term proportional to \( \rho^{-2} \) and a diagonal kinetic energy coupling term. At large \( \rho \), the potential is double-welled and its eigenvalues correlate to reactant and product vibrational states which are designated by \( R_n \) and \( P_n \), respectively, in the figure. In this region, the corresponding vibrational eigenfunctions are localized in
either the reactant or product valley. The diagonal dashed line represents the height of the barrier between the wells and approximately marks the boundary of the critical region of the potential energy surface. At values of $p$ within the dashed line, the vibrational wavefunctions expand to cover all of the critical region and to some extent lose their identification with reactants or products. This region is where the coupling between the adiabatic curves is localized. The $\text{RO}$ curve which correlates to $\text{H}_2 \ (v = 0)$ is predominantly coupled to the two closest curves which correlate to $\text{HF} \ (v = 2)$ and $v = 3$. The hyperspherical picture therefore neatly explains the product vibrational inversion. Reactive resonances are also conveniently visualized. $\text{RO}$ supports a quasi-bound state at the same energy as the spike in the $v = 2$ reaction probability shown in figure 1. A collision at this energy can access the quasi-bound state by tunneling through the barrier on the $\text{RO}$ curve, and reaction occurs by subsequent decay to the $\text{P}_2$ curve leading to $v = 2$ product. Although the $\text{HF}(v = 3)$ state is an energetically accessible decay product of this resonance, the height and width of the $v = 3$ adiabatic barrier on M5 results in the exclusive formation of $v = 2$.

This view of the resonance is slightly oversimplified. A comparison of the wells and barriers on $\text{RO}$ and $\text{P}_3$ with the true adiabatic wells and barriers found by Pollak$^{33}$ shows that while the heights and locations of the barriers more or less agree, the true $v = 3$ adiabatic well is substantially lower than on $\text{P}_3$. Another set of hyperspherical curves has been calculated by Romelt$^{40}$ with the origin at $\overline{Ra} = \overline{rA} = 0$ instead of that shown in figure 2. Romelt's barriers are similar to
these on R0 and P3, but his R0 and P3 curves cross inside the critical region and the P3 curve is the one that supports the quasi-bound state (see figure 7 in his paper) which in this case is confined by the P3 barrier. The conclusion to be drawn here is that the strong coupling inside the critical region causes the adiabatic wells to lose some of their physical significance. The lowest quasi-bound state is probably best described as having R0 and P3 character and, more importantly, as being confined within the critical region by the R0 barrier on the reactant side and the P3 barrier on the product side. It is therefore quite similar to the classical PODS corresponding to the lowest energy resonance.35

In order to relate dynamical resonances to experimental observables, it is necessary to consider the results of approximate three-dimensional quantal reactive scattering calculations on M5.29,41,42 In these calculations, the total and partial reactive cross sections do not show any sharp structure as the collision energy is varied. There are two effects to be considered when comparing collinear and three-dimensional resonances. The first is that the energy of the quasi-bound state will be higher in the 3-D case by the additional zero-point energies of the \( \text{FH}_2 \) bending modes. The second, more important, effect is the contribution of collisions with nonzero orbital angular momentum to the reaction. A quasi-bound state formed by a collision of orbital angular momentum \( L \) will have rotational energy on the order of \( B L (L + 1) \), where \( B \) is the rotational constant of the complex. If an \( L = 0 \) resonance occurs at energy \( E_0 \), then at approximately \( E_0 + B L (L + 1) \) a quasi-bound state can be formed by a collision of
orbital angular momentum $L_h$. Consequently, as the collision energy is increased beyond $E_0$, collisions with progressively larger values of orbital angular momentum will be brought into resonance. The large number of partial waves involved in reactive scattering allows the resonance to be accessed over a wide energy range. Thus resonances appear as broad, smooth features in the collision energy dependence of the total cross section which are difficult to distinguish from the substantial contribution from direct scattering.

Although reactive resonances cannot be observed in a state-resolved total cross section measurement, they can be seen in a reactive scattering experiment in which state-resolved differential cross-sections are determined. Classical\textsuperscript{17} and quasi-classical\textsuperscript{43,44} trajectory studies on $\text{M}_5$ show that the HF product angular distribution is dominated by backward scattering at $180^\circ$ with respect to the incident F beam up to collision energies of 5 kcal/mole. This is clearly related to the entrance channel properties of the potential energy surface which favors collinear, low impact parameter approach of the reactants. The quantal calculations, predict, however, that as the collision energy is raised from 2 to 3 kcal/mole, the $v = 2$ distribution shifts from backward-peaked to sideways-peaked, whereas the $v = 3$ distribution remains backward-peaked. This is attributed to dynamical resonance effects. As the collision energy is raised, quasi-bound states are formed by progressively higher impact parameter collisions, and their subsequent decay to $v = 2$ product leads to a state-selective broadening of the $v = 2$ angular distribution. The shift in the $v = 2$ distribution will be even more pronounced if the lifetime of the quasi-bound state.
is an appreciable function of the rotational period of the complex. The experimental determination of the angular and kinetic energy distributions for each product vibrational state therefore offers the most promise for characterizing resonances in reactive scattering.

Earlier molecular beam work carried out in our laboratory in search of resonances in F + H\textsubscript{2} showed that the HF v = 2 angular distribution did broaden and exhibit slight sideways-peaking as the collision energy was raised from 2-3 kcal/mole, but the results for v = 3 were inconclusive as the limited range of our angular scan due to the high m/e=20 background near the F beam precluded the observation of possible sideways or forward-scattered v = 3 product at any energy.\textsuperscript{45,46} This was a serious shortcoming because, without this information on the v = 3 product, the state-specificity of the v = 2 sideways-peaking could not be confirmed. The case for a resonance is much stronger if a clear state-specific effect can be found. In order to remedy this limitation, several modifications to the apparatus were made recently which permit the scattering of the product vibrational states to be much better-resolved and allow the determination of a complete differential cross section for the v = 3 product. This chapter discusses the results for F + p-H\textsubscript{2} and F + n-H\textsubscript{2} at collision energies ranging from 0.7 to 3.5 kcal/mole. Some of the F + p-H\textsubscript{2} work has been discussed previously,\textsuperscript{47} and the following chapter reports on our studies of the F + D\textsubscript{2} and F + HD reactions.
Experimental

Figure 4 shows a top cross sectional view of the experimental arrangement. The F and H$_2$ beams with FWHM angular spreads of 2° and 3°, respectively, intersected at 90° inside a vacuum chamber where the pressure was $7 \times 10^{-7}$ torr with both beams on. The collision region defined by the intersection of the two beams was about 0.080" on a side. The scattered HF product was detected by a rotating ultra-high vacuum mass spectrometer consisting of an electron-impact ionizer, a quadrupole mass spectrometer, and a Daly detector for ion counting. The detector was triply-differentially pumped in order to reduce the partial pressure of background gas at the ionizer.

Most of the details concerning the construction of the apparatus and detector have been given elsewhere. However, several modifications were made specifically for these studies. The major objective was to reduce the velocity spread of the reactant beams in order to resolve the product vibrational states as distinct peaks in time-of-flight measurements at as many angles as possible. In our earlier work on F + H$_2$, the limiting factor in the time-of-flight resolution was not the center-of-mass energy spread of the reactants, but rather the spread in the velocity of the center-of-mass in the LAB frame which primarily results from the F beam velocity distribution. In order to improve on this, a velocity-selected effusive F beam was used which had a considerably narrower velocity spread than the supersonic beams seeded in N$_2$ or Kr in the previous work. The loss of intensity from using a velocity-selected beam was compensated for by increasing the H$_2$ intensity at the interaction region and
decreasing the m/e = 20 background caused by doubly-ionized residual Ar in the detector and HF produced inside the F source chambers.

The F atom beam was produced by thermally dissociating pure F₂ in a resistively heated Ni oven. The small amount of HF in the F₂ was removed first by passing it through a bakeable NaF trap and then a liquid nitrogen trap before admitting it to the oven. The F₂ pressure was 2.0 torr and the oven temperature was 650°C. This resulted in about 50% dissociation of the F₂. The gas exited the oven through a 0.060" x 0.070" aperture into a source chamber where the pressure was maintained at about 10⁻⁴ torr during operation of the source. A collimated beam was formed by a 0.050" x 0.060" defining slit located 0.5" from the oven exit aperture. This slit separated the source chamber from a differential pumping chamber which housed the velocity selector and was maintained at 2 x 10⁻⁶ torr. The velocity-selected beam entered the main vacuum chamber through a second defining slit, a 0.050" x 0.060" aperture which was 1.0" from the collision region.

The angular divergence of the F beam as determined by the two defining slits was 2°.

The source chamber was pumped by a Varian HS-10 diffusion pump, and the differential chamber was pumped with a VHS-4 diffusion pump. Fomblin oil was used in both pumps to minimize HF formation on the chamber walls. The mechanical pump backing the source diffusion pump also used Fomblin oil which was continuously purified of HF by an external oil filter. The mechanical pump ran without breakdown even though several pounds of F₂ passed through it in the course of the experiment.
The F oven was constructed by concentrically welding two sleeves of nickel tubing to a disk with the exit aperture at its center. The wall thickness of both sleeves was 0.065". The inner sleeve was 0.75" O.D. and 8.5" long and eventually connected to the F₂ feed line. The outer sleeve was 1.0" O.D. and 2.5" long. Most of the outer sleeve was machined to 0.020" wall thickness and a tight-fitting, 0.25" wall thickness, 1.5" long Ni cylinder was welded to the outside of the inner sleeve just behind the outer sleeve. These steps were taken to achieve uniform heating of the inner sleeve for several inches behind the exit aperture. Water-cooled copper electrodes were clamped to the end of each sleeve. The oven required 400 A at 1V from an AC power supply to reach 650°C. The gas pressure in the oven was measured with a capacitance manometer, and the temperature was monitored by Chromel-Alumel thermocouples spot-welded to the oven in several places. Each oven was passivated just after installation in order to retard deterioration of the oven at high temperature. In this procedure, F₂ was passed through the oven at room temperature for one hour. The gas flow was stopped and the oven temperature was raised 100°C and left for one hour. F₂ gas was then admitted for one hour at the higher temperature. The procedure was continued in 100°C increments until the operating temperature of the oven was reached. The idea was to form a uniform and dense NiF₂ coating inside the oven to protect it from attack by fluorine at 650°C.

From our experience, when a smaller oven is used, the dissociation of F₂ in the oven is limited by the average residence time of the gas in the hot part of the oven rather than the dissociation constant.
at the oven temperature. We sought to maximize the residence time in order to achieve chemical equilibrium by using an oven with larger volume and by taking the steps described above to insure an extended, uniformly hot region behind the exit aperture. If any part of the inner sleeve was heated above 700°C, the NiF₂ coating boiled off and rapidly clogged the first defining slit which was at room temperature. The deterioration of the oven was also accelerated. Each oven lasted several months under the operating conditions described above, the only maintenance being periodic cleaning of the first defining slit.

The velocity selector consisted of six aluminum alloy wheels, each of which was 7" diameter, 0.040" thick, and had 180 slots 0.065" wide and 0.3" deep. The distance from the first to last wheel was 1.41". The configuration of the selector was taken from Steyn and Verster⁵¹ and gave a FWHM velocity spread of 11% for the F beam. The selector was spun at 500 Hz and the resulting most probable F beam velocity was 8.7 x 10⁴ cm/sec. The wheel assembly was mounted on two bearings and connected to a three phase synchronous motor⁵² by a flexible coupling shaft.⁵³ Barden SR4SSTA5 bearings coated with Bray 3L-38 grease⁵³ᵃ were used for the wheel assembly and inside the motor. The motor was powered by a three-phase supply of our own design. The frequency of the spinning wheels was monitored by a slotted optical switch containing an LED and a phototransistor.⁵⁴ The wheel assembly and motor were clamped to an aluminum base which was bolted to the bottom of the differential chamber. It was necessary to dynamically balance each wheel separately as well as the entire assembled selector to achieve smooth operation at 500 Hz.
Early attempts to study the F + H₂ reaction with this source configuration were frustrated because of the high rate of effusion of HF which formed in the differential region and entered the main chamber via the 2nd defining slit. The velocity selector only permitted about 1% of the effusive beam to pass through it, and the remaining F atoms were free to collide with the chamber walls and eventually form HF. We constructed a liquid nitrogen-cooled cold shield inside the differential region consisting of several large 1/8" copper plates in order to maximize HF cryopumping. One plate was located between the velocity selector and the 2nd defining slit and admitted the beam through a 9/32" hole. The cold shield and the use of Fomblin pump oil virtually eliminated effusive HF background at angles greater than 10° away from the F beam.

The supersonic H₂ beam was produced by expanding pure H₂ through a 70 μ orifice into a source chamber. The orifice was 0.4" from the tip of a nickel skimmer with an entrance hole of 0.018" diameter.⁵⁶ The beam, which was essentially defined by the nozzle and skimmer geometry, then entered the main chamber; no differential region was used for the H₂ source in order to minimize the distance between the source orifice and the collision region. An 0.080" collimating slit in the main chamber between the skimmer and the interaction region prevented background H₂ in the source chamber from effusing through the skimmer and directly intersecting the F beam outside the collision region.
The source was fabricated by brazing a platinum electron microscope aperture with a 70 µ orifice \textsuperscript{56} to a copper tube. The tube had several turns of coaxial heater \textsuperscript{57} brazed to it as well as a liquid nitrogen contact. The source temperature could be varied continuously from 90°K to 720°K. This gave a collision energy range from 0.7 to 4.5 kcal/mole. The source temperature was monitored by a Chromel-Alumel thermocouple clamped to the tube just behind the orifice. The thermocouple was connected to a temperature control unit of our own design which regulated the voltage across the heating coil. The H\textsubscript{2} source chamber was pumped by a Varian VHS-400 diffusion pump with a nominal pumping speed of 8000 liter/sec which was backed by a 330 CFM roots blower/mechanical pump combination. The operating pressure in the source was $6 \times 10^{-4}$ torr. Typical H\textsubscript{2} stagnation pressures were 80 psi at room temperature, 120 psi at 720°K, and 45 psi at 85°K. Matheson Ultra-High Purity H\textsubscript{2} (99.999% pure) was used for the n-H\textsubscript{2} experiments. The para-H\textsubscript{2} was made in the Low Temperature Laboratory of the Berkeley Chemistry Department and stored in aluminum tanks at 200 psi. Previous photoelectron spectroscopy work showed that para-H\textsubscript{2} stored in this manner lasted 1-2 weeks without significant conversion.

In the original configuration of the detector, each of the three differential regions was pumped by a 200 l/sec ion pump. For this experiment, in order to reduce the rare gas background, the ion pumps were chemically cleaned and baked out into a turbomolecular pump prior to mounting them onto the apparatus. The rare gas pumping capability
of the detector was further improved by adding a 110 l/sec turbomolecular pump to the outermost region and a 330 l/sec turbomolecular pumped backed by a 110 l/sec turbo-pump to the 2nd region. The two 110 l/sec pumps exhausted into the main chamber. The turbomolecular pumps could be isolated from the detector with all-metal valves so that routine maintenance could be performed on them without venting the detector. The resulting reduction in the mass 20 background was substantial. With the detector isolated from the main chamber, the mass 20 background count rate under normal detector operating conditions was 150 Hz. The count rate observed before the turbomolecular pumps were installed was never below 800 Hz.

Angular scans of the HF product were taken by modulating the \( H_2 \) beam with a 150 Hz tuning fork chopper and recording the modulated HF signal as a function of angle. The chopper was located in the main chamber between the skimmer and the collimating slit and could be moved out of the path of the \( H_2 \) beam for time-of-flight measurements. Typical counting times were 266-532 seconds at each angle which yielded error bars of less than 3\% except at the lowest collision energies. The angular resolution of the detector was 1.25\(^\circ\), and points were taken every 2\(^\circ\) except near the F beam where they were taken at 1\(^\circ\) intervals.

Time-of-flight measurements were performed on both beams to characterize their velocity distributions, and on the HF reactive scattering product. The TOF wheel and motor assembly was bolted to the rotating detector. For the analysis of the beam velocity distributions, TOF measurements were done using a 7" diameter stainless
steel wheel with 4 equally spaced 0.010 mil slots. The wheel was spun at 300 Hz. A multichannel scaler connected to an LSI 11 microcomputer controlled the data acquisition. Typical channel widths were 1 µsec for the H₂ beam and 2 µsec for the F beam. The H₂ beam time-of-flight measurements were deconvoluted to account for the length of the ionizer and other broadening effects. The resulting velocity distributions had typical FWHM spreads of 3 percent. TOF measurements on the F beam confirmed that its peak velocity was identical to that expected from the velocity selector design parameters. The F beam velocity showed no detectable variation over the course of the experiment even though the velocity selector was removed and replaced several times. This was a welcome change from the earlier studies with supersonic F beams where the size of the source orifice would change over time and alter the beam characteristics. As the F beam velocity has a large effect on the kinematics of this reaction, the constant velocity was yet another advantage gained by using a velocity-selected beam. The spread in center-of-mass collision energies due to the beam velocity distributions was about 0.1 kcal/mole.

The HF product velocity distribution was determined using cross-correlation TOF method due to the low signal intensity. A 7" Be-Cu wheel with a 255 element pseudorandom sequence photoetched into it was used. The wheel was spun at 490 Hz which corresponded to 8 µsec/channel resolution in the TOF spectra. Typical TOF counting times were 1-2 hours. Spectra were taken every 2° where the signal was more intense and at larger intervals at angles far from the F beam where the lower signal necessitated longer counting times.
Results

A. Product Angular Distributions

Measurements of the product angular distributions were taken at several collision energies for $F + p-H_2$ and $F + n-H_2$. The $H_2$ source conditions for each energy are displayed in table I. The $H_2$ stagnation pressure was adjusted so that the pressure in the main chamber was the same at all energies with the $H_2$ beam on. In order to obtain the same beam velocities for $n-H_2$ and $p-H_2$, it was necessary to run the $n-H_2$ at a slightly higher temperature. This was expected, as more rotational relaxation can occur in a supersonic expansion of $p-H_2$ than for $n-H_2$ in the temperature range we studied because $H_2$ can undergo only even $\Delta J$ rotational transitions. For example, at 304°K, 79% of the $n-H_2$ is in $J = 0$ or $J = 1$ and cannot relax any further. On the other hand, 51% of the $p-H_2$ is in $J = 0$, and the remaining 49 percent of the molecules, all of which are in even $J$ states and most of which are in $J = 2$, can in principle relax to $J = 0$ and increase the beam velocity in the process. Photoelectron spectroscopy on supersonic molecular beams of $p-H_2$ and $n-H_2$ shows that substantial relaxation does occur;61 more than 80% of the $p-H_2$ ends up in $J = 0$ under our operating conditions. Although the $F + p-H_2$ and $F + n-H_2$ angular distributions at the same collision energies were quite different for $E \leq 1.84$ kcal/mole, no difference was observed at the higher energies where it was necessary to heat the nozzle above room temperature. This may have been due either to a large amount of rotationally excited $p-H_2$ remaining after the expansion, or to wall-catalyzed para $\rightarrow$ ortho conversion at the higher temperatures. In any case no data for high temperature $F + p-H_2$ reactions are reported here.
The HF product angular distribution for $F + p-H_2$ at 1.84 kcal/mole is shown in figure 5. The LAB angle $\theta$ is measured from the F beam. The laboratory angular distribution shows considerable structure which can be related to the important features of the product velocity and angular distributions in the center-of-mass frame of reference with the aid of the Newton diagram below the scan.

The Newton diagram shows the relationship between the LAB and CM velocity vectors. $v_F$ and $v_{H_2}$ are the LAB reactant velocities, and the CM reactant velocities are $u_F$ and $u_{H_2}$ ($u_{H_2}$ is not drawn to scale). The origin in the center-of-mass coordinate system is the tip of the vector representing the velocity of the center-of-mass in the LAB frame. The angle between this vector and $v_F$ is labelled $\theta_{cm}$. $\theta = 0^\circ$ in the center-of-mass frame is defined as the direction of the incident $F$ beam in the center-of-mass coordinate system. HF product scattered near $\theta = 0^\circ$ in the center-of-mass is referred to as forward-scattered, while HF scattered near $\theta = 180^\circ$ is termed backward-scattered. The 'Newton circles' show the maximum CM speed for HF product formed in the indicated vibrational state and therefore delineate the LAB angular range over which each state will be observed.

The peaks in the angular distribution occur at LAB angles where the LAB velocity vector is nearly tangent to a Newton circle. The broad peaks at $\theta = 28^\circ$ and $\theta = 45^\circ$ appear to be from backward-scattered $v = 3$ and $v = 2$ product, respectively. The sharp peak at $\theta = 8^\circ$ appears to be from forward-scattered $v = 3$. This prominent feature could not be clearly observed in our previous studies of $F + H_2$. In the work using a supersonic beam of $F$ in $N_2$, $v_F$ was considerably
faster than in this experiment. $\Theta$ cm was therefore much smaller, and any forward scattered $v = 3$ product would have been so close to the $F$ beam that it would have been obscured by HF impurity in and near the beam. In the studies where $F$ was seeded in Kr carrier gas, elastically scattered $^{80}\text{Kr}$ which was ionized to $\text{Kr}^{4+}$ interfered with the observation of reactively scattered HF near the $F$ beam. In the current configuration any forward scattered $v = 2$ would have been on the other side of the $F$ beam, but still within the angular range of the rotatable detector. No evidence of forward-scattered $v = 2$ was observed at any collision energy.

The angular distributions for $F + n$-$\text{H}_2$ and $F + p$-$\text{H}_2$ are shown in figures 6 and 7. The scans were taken on different days, and some variation in experimental conditions unavoidably occurred. This was mostly due to the variation of the $F_2$ dissociation ratio resulting from running the $F$ oven at slightly different temperatures. However, we spent one day measuring representative angles at each collision energy so that the complete angular distributions could be correctly scaled for constant $F$ and $\text{H}_2$ flux. The scaling factors obtained by this procedure are listed in table I. The only angular distributions that required substantial adjustment were the two lowest $F + p$-$\text{H}_2$ runs and $F + n$-$\text{H}_2$ at 0.68 kcal/mole.

The structure described above in the $F + p$-$\text{H}_2$ is evident in nearly all the angular distributions. The sharp forward $v = 3$ peak and broad backward $v = 3$ peak occur in every angular distribution, and the backward $v = 2$ peak is distinct except in the 0.68 kcal/mole measurements. Several noteworthy trends are evident. For both $F + p$-$\text{H}_2$
and \( F + n-H_2 \), the magnitude of the forward peak increases as the collision energy is raised except for \( F + p-H_2 \) at 1.0 kcal/mole where the scaling is more uncertain. For \( F + n-H_2 \) collision energies \( > 1.0 \) kcal/mole, the backward \( v = 3 \) peak decreases relative to the forward peak as the collision energy is raised. The same trend is seen in the \( F + p-H_2 \) scans at 1.30 and 1.84 kcal/mole. However, this trend reverses as the collision energy is lowered from 1.30 kcal/mole; the two lowest energy \( F + p-H_2 \) angular distributions show that the backward peak falls off faster than the forward peak as the energy decreases. For \( F + n-H_2 \), the low collision energy fall-off of the backward peak occurs only at 0.68 kcal/mole.

A comparison of the \( F + p-H_2 \) angular distributions with \( F + n-H_2 \) at the same collision energy shows the ratio of the forward-to-backward \( v = 3 \) peak heights to be considerably larger for \( F + p-H_2 \). The high quality of the data at 1.84 kcal/mole allows the determination of the \( F+H_2 \) \((J = 1) \) LAB angular distribution using the formula

\[
N_{J=1}(\theta) = 4/3 \left( N_{n-H_2}(\theta) - \frac{1}{4} N_{p-H_2}(\theta) \right).
\]

This formula is exact if the even \( J \) distributions are the same in \( n-H_2 \) and \( p-H_2 \), and all the odd \( J \) rotational population of the \( n-H_2 \) is in \( J = 1 \). Pollard's results show these are both very reasonable assumptions; 95% of the odd \( J \) population should be in \( J = 1 \) under our operating conditions. The \( J = 1 \) and \( J = 0 \) scans are shown in figure 8. The forward peak is lower in the \( J = 1 \) distribution, whereas the backward \( v = 2 \) and \( v = 3 \) peaks are higher. In addition, the \( v = 3 \) signal for \( J = 1 \) spans a slightly wider LAB angular range. The \( v = 3 \) Newton
circle for $F + H_2$ ($J = 1$) is slightly larger than for $F + H_2$ ($J = 0$) because of the additional $H_2$ rotational energy. The figure therefore shows that some of the rotational energy ends up as product recoil energy.

B. Time-of-Flight Measurements of Velocity Distributions

In order to determine the product velocity distributions, time-of-flight spectra were taken at $E = 1.84$ kcal/mole for $F + p-H_2$, and at $1.84, 2.74$ and $3.42$ kcal/mole for $F + n-H_2$. About 20-25 spectra at different angles were taken at each energy. The spectra for all four systems are shown in figures 9 to 12.

The TOF spectra show distinct peaks which correspond to various product vibrational states. The peaks are well-separated because of the narrow beam velocity distributions and the fact that product rotational excitation is small relative to the spacing between the vibrational energy levels of the HF product. Each spectrum allows one to quantify the contribution of the individual product vibrational states to the total signal at that LAB angle.

The spectrum at $\theta = 18^\circ$ for $F + p-H_2$ at 1.84 kcal/mole (figure 9a) shows the degree of resolution obtained in these measurements. This angle is close to $\theta_{CM}$ at this energy. The fastest peak is from $v = 2$ product, and the two slower peaks are from $v = 3$. Most of the $v = 3$ product flux occurs just inside the $v=3$ Newton circle, so the $v = 3$ product is sampled in two distinct regions of LAB velocity space at $\theta = 18^\circ$ which results in two peaks appearing in the TOF spectrum. In this spectrum, the two $v=3$ peaks represent scattering
at nearly the same angle in the center-of-mass. Although scattering in the center-of-mass has cylindrical symmetry about the reactant relative velocity vector, the slower peak is smaller because it is spread out over more time-of-flight channels. This is reflected in the conversion from CM velocity flux to LAB number density at arrival time $T$ which is proportional to $T^{-3.46}$. The slow peak expected for the $v=2$ state is affected even more strongly by this factor and is often not clearly seen in the TOF spectra. The two $v=3$ peaks merge at LAB angles that are nearly tangent to the $v=3$ circle. The spectra at $\theta = 8^\circ$ and $\theta = 30^\circ$ for $p-H_2$ are examples of this. The spectrum at $\theta = 8^\circ$ confirms that the peak in the angular scan is from $v=3$ product. The spectra at larger LAB angles show a contribution from the $v=1$ product that is, at least in some cases, distinct from the $v=2$ peak. The resolution in the TOF spectra at higher energies is somewhat worse, but resolved peaks are still evident in all the spectra even at 3.42 kcal/mole.

TOF spectra at angles $\theta \leq 10^\circ$ were contaminated to some extent by slow, effusive HF originating from the differential pumping chamber of the F beam source. The contribution from the effusive component was determined by flagging the F beam and taking a spectrum at $\theta = 4^\circ$ where the effusive signal was quite intense. This spectrum was scaled to fit the slow tail in the reactive TOF spectrum and subtracted. Figure 13 shows the raw data at $\theta = 8^\circ$ for $F + p-H_2$, the scaled effusive TOF, and the result from the subtraction. The contribution from the effusive component is considerably smaller at $10^\circ$ and is insignificant at $12^\circ$. 
Analysis

Center-of-mass product angular and translational energy distributions were obtained for the four energies studied by product time-of-flight measurements. The distributions were determined by forward convolution. A trial CM angular and energy distribution for each vibrational state was input to a computer program. The program performed the necessary CM → LAB transformations and averaged over the beam velocity distributions and detector resolution in order to generate a LAB angular distribution and TOF spectra. The CM parameters were varied until the computer-generated results matched the data. The best fits to the four LAB angular distributions are shown in figures 5 and 14-16, and the fits to the TOF spectra can be seen in figures 9-12.

The coupled CM angular and energy distributions are of the form:

\[ P_i(E, \theta) = N_i A_i T_i(\theta) \left( \frac{E}{E_{i1}} \right)^{\alpha_i(\theta)} (1 - E/E_{i1})^{\beta_i(\theta)} \]  

(1)

where

\[ \beta_i(\theta) = \alpha_i(\theta) (E_p(\theta)/(1-E_p(\theta))). \]  

(2)

Here \( i \) is the product vibrational state, \( E \) is the product recoil energy, and \( E_{i1} = \Delta E + E_{\text{coll}} - E_i \) is the maximum recoil energy for product in the \( i \)th vibrational state. \( \Delta E \) is the exothermicity, \( E_{\text{coll}} \) is the collision energy, and \( E_i \) is the vibrational energy of HF(\( v = i \)) relative to HF(\( v = 0 \)). The energetics for the F + H\(_2\) reaction are shown in figure 17.12 For F + p-H\(_2\), the exothermicity used in the data fitting was 32.17 kcal/mole. For F + n-H\(_2\), most of the H\(_2\) was in J = 1 and this rotational excitation was added to the exothermicity to give \( \Delta E = 32.51 \) kcal/mole.
The adjustable parameters are $A_i$, an overall intensity factor, $T_i(\phi)$, the intensity at CM angle $\phi$, $E^i_p(\phi)$, the peak in the angle-dependent recoil distribution at $\phi$ (expressed as a fraction of $E^i_m$), and $\alpha_i(\phi)$ which determines the width of the energy distribution. $N_i$ is a normalization factor given by

$$N_i = \left[ E^i_m B(\alpha_i(\phi), 1, \beta_i(\phi) + 1) \right]^{-1}$$

(3)

where $B(a,b) = \frac{\Gamma(a) \Gamma(b)}{\Gamma(a + b)}$.

This insures that

$$\int_0^{E^i_m} P_i(E, \phi) \, dE = A_i T_i(\phi) = I_i(\phi)$$

(4)

which is the total intensity for state $i$ at $\phi$. The angle-dependent parameters were input in point form every $5^\circ$ and their values at intermediate angles were obtained by linear interpolation.

The spread in the F beam velocity was by far the most important averaging factor in the forward convolution and it required careful characterization. The transmission function $B(v)$ for a perfectly collimated beam with no angular divergence has been given elsewhere.\cite{63} This should, in principle, be convoluted with the velocity distribution of the F atoms emerging from the oven over the range of transmission in order to obtain a realistic estimate of the F beam velocity distribution. We found this unnecessary, however, as $v_F = 8.7 \times 10^4$ cm/sec is close to the maximum of the Maxwell-Boltzmann distribution at $920^\circ\text{K}$ where the intensity variation is insignificant.
over the transmission window of the velocity selector. A larger effect arises from the angular divergence of the F beam. As shown in figure 4, the beam passes through the side of velocity selector, where the wheel slots are parallel to the scattering plane, rather than through the top of the selector. The angular divergence in the scattering plane does not affect the transmission function of the velocity selector, although it does affect the Newton diagram for the reaction and is accounted for in the analysis program. However, for an out-of-plane trajectory through the velocity selector, the transmission function will be somewhat different. Frank has derived an expression for $B(v,\alpha)$, the dependence of the transmission function on the angular deviation $\alpha$ from an in-plane trajectory. The out-of-plane divergence of the F beam was 2°, and the angular offset between the first and last wheel was 17.3°. $B(v,\alpha)$ must be multiplied by the angular transmission function of the two defining slits for the F beam which is approximately triangular and is given by

$$T(\alpha) = 1 - \frac{|\alpha|}{\alpha_{\text{max}}}$$

(5)

where $\alpha_{\text{max}} = 1°$ in this case. The angle-averaged transmission function of the selector is then

$$B(v) = \int_{-\alpha_{\text{max}}}^{\alpha_{\text{max}}} T(\alpha) B(v,\alpha) \, d\alpha.$$  

(6)

This increases the FWHM of the velocity selector from 11% to 12.6 percent and has a small but noticeable effect on the calculated TOF distributions. One interesting point regarding this correction is that it is underestimated in the F beam TOF measurements. These are
taken with a 0.005" hole in front of the detector to limit the gas flow when the detector is looking directly into the beam. This greatly restricts the angular range of the trajectories entering the detector. Consequently, the width of the measured TOF spectrum of the beam is very close to that expected from the velocity selector with a perfectly parallel beam.

The time-of-flight spectra for all four energies show a common feature at LAB angles which sample \( v=3 \) scattered near \( 180^\circ \) in the center-of-mass coordinate. The spectrum for \( F + p-H_2 \) at \( \Theta = 30^\circ \) is a good example. The faster peak is from \( v = 2 \). The slower peak corresponding to \( v = 3 \) has a fast shoulder which exceeds the exothermicity for the \( v = 3 \) product. In order to fit this, it was necessary to postulate another 'state' corresponding to \( HF(v = 3) \) formed from reactants with about 1 kcal/mole internal excitation. This state is labelled \( v = 3' \) in the figures. The possible sources for this extra energy are contributions to the reaction from spin-orbit excited \( F(^2P_{1/2}) \) or rotationally excited \( H_2 \). The \( F(^2P_{1/2}) \) state lies 1.16 kcal/mole above the \( (^2P_{3/2}) \) ground state and constitutes 21 percent of the \( F \) beam assuming thermal equilibrium at 920°K. \( H_2(J = 2) \) is 1.03 kcal/mole above \( J=0 \) and makes up 20 percent of the \( p-H_2 \) beam. The energy difference between these two alternatives is too small to be resolved in our TOF analysis. For \( n-H_2 \), the situation is somewhat different. The exothermicity includes the rotational energy of \( H_2(J = 1) \), and the \( J = 2 \) state is only 0.68 kcal/mole higher. However, for \( n-H_2 \) the \( J = 3 \) population is close to the \( J = 2 \) population and reaction from this state may also be occurring. Indeed, the
problematic peaks in the F+n-H$_2$ spectra could be better fit assuming
1.16 kcal/mole excitation for the v = 3' state than with 0.68 kcal/mole,
and the higher value was used in the final fit. The selected value for
the energy of the v = 3' state therefore does not resolve the issue of
the source of the excitation. The partial cross section results for
each vibrational state presented below, on the other hand, support
the hypothesis that v = 3' is from rotationally excited H$_2$.

Due to their large number, the best fit CM parameters are graphically
displayed in figures 18-21 rather than explicitly listed. The
top graph in each of these figures is the most interesting, as it shows
the vibrationally state-resolved CM differential cross sections given
by eq.(4), as well as the summed differential cross section $\sum_i I_i(\theta)$. Center-of-mass velocity flux contour maps as a function of scattering
angle are shown in figures 22-25. These are contours of the function,
$\sum_i uP_i(E(u),\theta)$, where $u$ is the HF product CM speed, plotted on a
polar (u,\theta) coordinate system. Below each map is a 3-D perspective
which especially aids in viewing the v = 3 forward peak. The contour
maps, in general, confirm the qualitative trends inferred from the LAB
angular scans. The intensity of the v = 3 peak increases with collis-
ion energy and is higher for F + p-H$_2$ than for F + n-H$_2$ at the same
energy. No backward peak for v = 3 is observed at any energy; the
broad peak in the LAB angular distributions results from sampling more
v = 3 product at LAB angles nearly tangent to the v = 3 circle than at
LAB angles closer to the F beam. It is clear, however, that the amount
of v = 3 scattered at $\theta > 90^\circ$ decreases with increasing energy. The
maps show the v = 2 and v = 1 product is scattered predominantly in
the backward hemisphere. The \( v = 2 \) product is backward-peaked at 1.84 kcal/mole and shows slight sideways peaking at the higher energies. The sideways-peaking at higher energies was also seen in our earlier investigations. The \( v = 1 \) product distributions, especially at 1.84 kcal/mole, are less reliable than those for the other states due to the low intensity of that state in the LAB frame. The \( v = 3 \) product is scattered entirely into the backward hemisphere. However, any forward-scattered \( v = 3 \) at CM angles \( < 30^\circ \) would be closer than \( \Theta = 8^\circ \) to the F beam. We could not obtain reliable TOF data at LAB angles smaller than \( 8^\circ \) because the effusive contribution to the total signal was too large. The possibility of a narrow forward \( v = 3 \) peak therefore cannot be ruled out. The assessment of the contribution from this state is less reliable at the higher energies where the \( v = 2 \) and \( v = 3 \) peaks are less well-resolved. In general the data was fit using as little \( v = 3 \) as possible, so all the fits, especially those at higher energy, probably underestimate the \( v = 3 \) contribution.

The kinetic energy distributions for each vibrational state as a function of scattering angle can be converted into HF rotational population distributions. The recoil energy, \( E \), and the product rotational energy, \( E_R \), for vibrational state \( i \) are related by

\[
E = \Delta E + E_{\text{coll}} - E_i - E_R \tag{7}
\]

For a fixed CM angle, the recoil energy distribution is given by
\[ P(E) = P(E_{m}^{i} - E_{R}), \quad (8) \]

and

\[ P_{c}(J) = P(E) \frac{dE}{dJ} = 2B_{i}(J+1/2)P(E_{m}^{i} - B_{i}J(J+1)) \quad (9) \]

is the distribution function for the continuous variable \( J \). Here \( B_{i} \) is the rotational constant for vibrational state \( i \). The discrete populations can be derived by what amounts to a quasi-classical approximation:

\[ P(J) = \int_{J}^{J+1} P_{c}(J') \, dJ' \quad (10) \]

Some sample population distributions are shown in figure 26. Figures 27–30 show plots of the fraction of available energy appearing as product rotation, \( <F_{J}>_{i} \), and the mean rotational quantum number, \( <J>_{i} \), as a function of CM scattering angle for each product vibrational state. These are obtained from the continuous recoil energy distributions by:

\[ <F_{J}>_{i} = 1 - \int_{0}^{E_{m}^{i}} \left( \frac{E}{E_{m}^{i}} \right) P_{i}(E, \theta) \, dE \quad (11) \]

\[ <J>_{i} = \int_{0}^{E_{m}^{i}} J_{i}(E) \, P_{i}(E, \theta) \, dE \quad (12) \]

Here \( J_{i}(E) \) is implicitly defined by

\[ E_{m}^{i} - E = B_{i}J(J+1). \quad (12b) \]

Note that \( <F_{J}>_{i} \) is a state-specific quantity that indicates how much energy not already tied up in vibration occurs as product rotation. It is not the same as the more commonly used symbol, \( <f_{R}> \), which is the fraction of the total available energy appearing as product rotation.
The validity of this procedure is limited to a certain extent by several factors which derive from our inability to resolve individual rotational states. There is a certain amount of ambiguity in transforming a continuous to a discrete distribution, and the shape of the discrete distribution is determined by the functional form assumed for the continuous distribution. Another problem is that the exothermicity used to derive the amount of product rotational energy depends on the reactant rotational state. The values used were for the dominant rotational state, just as in the fitting procedure for the CM scattering. Thus, for example, the contribution to reaction from the 20-25 percent of the n-H₂ beam in J = 0 is not treated explicitly. Nonetheless, the v = 2 rotational distributions at 1.84 kcal/mole are similar to the most recent chemiluminescence results at an average collision energy of 1.5 kcal/mole. This indicates that even if the individual state populations are not directly determined, our high resolution experimental results provide a reasonable estimate of the product rotational distributions as well. The relative heights and positions of the two v = 3 peaks observed in many of the TOF spectra are quite sensitive to the details of the assumed kinetic energy distribution and this state is therefore better-characterized than the v = 2 state.

Several trends are apparent in the distributions. For each energy, the rotational distribution of the v = 3 state gradually shifts towards lower J at smaller CM angles, and more abruptly near 0°. A comparison of the three F + n-H₂ energies shows that, in general, <J> increases for the v = 2 and v = 3 products as the
collision energy is raised. The only exception to this is in the neighborhood of 0° where $\langle J \rangle$ decreases at higher collision energies. The $F + n$-H$_2$ distribution shows more rotational excitation than $F + p$-H$_2$ at the same collision energy. This agrees with earlier chemiluminescence work.

The plots of $\langle F_J \rangle$ for each $F+n$-H$_2$ collision energy show quite different behavior for the $v = 2$ and $v = 3$ states. While $\langle F_J \rangle$ for $v = 2$ steadily increases with collision energy, for the $v = 3$ state it is less at most angles at 2.74 kcal/mole than at 1.84 kcal/mole, and the $v = 3$ results at 3.42 kcal/mole are similar to those at 2.74 kcal/mole. This indicates that reactant translational energy is channeled more efficiently into rotational excitation of $v = 2$ product than $v = 3$ product.

We have also computed relative partial cross sections for each product state from the CM parameters. These are given by

$$\sigma_i = 2\pi \int_0^\pi I_i(\theta) \sin \theta d\theta$$

$$= \sum_{j=1}^{36} \int_{\theta}^{\theta+1} I_{ij}(\theta) \sin \theta d\theta$$

where

$$I_{ij}(\theta) = A_i \left( T_{ij} + T_{i(j+1)} \frac{\theta - \theta_j}{\theta_{j+1} - \theta_j} \right).$$

A factor of $2\pi$ is omitted for convenience as it has no bearing on the relative cross sections. $T_{ij}$ is the angular intensity for state which, as previously mentioned, is specified at 5° intervals. $T_{i1}$ is at 0° and $T_{i37}$ is at 180°. The result is given by
The relative total cross section is simply \( \sigma = \sum \sigma_i \). The \( v = 2 \) and \( v = 3 \) partial cross sections should be accurate to within a few percent. They are quite insensitive to changes in the CM parameters that are large enough to adversely affect the calculated fits to the LAB data.

The comparison of partial cross sections at different collision energies must be done with some care. The analysis program computes the signal at each LAB angle \( \theta \), from the CM distributions by

\[
S(\theta) = C \sum_{ijk} I_i(\theta) p_i(E,\theta) \frac{v_j}{E} p(v_{1k},v_{21})
\]

Equation (17) should be compared to the exact relation between CM differential cross sections and LAB number density.62

\[
\sigma_i = T_{i1} + T_{i37} + \sum_{j=1}^{36} \frac{T_{i(j+1)} - T_{ij}}{\Theta_{j+1} - \Theta_j} (\sin \Theta_{j+1} - \sin \Theta_j).
\]
Here \( n_1 \) and \( n_2 \) are the reactant number densities in the interaction, \( v_r \) is the reactant relative velocity, \( \Delta V \) is the volume of the interaction region, \( A \) is a constant incorporating the solid angle subtended by the detector, the detection efficiency, and various mass factors, and \( \frac{d^3\sigma_i}{d^3\omega dE} \) is the CM angular and kinetic energy double differential cross differential cross section for product vibrational state \( i \). This is related to our energy and angular distributions by

\[
\frac{d^3\sigma_i}{d^3\omega dE} = BC \ I_i(\theta) \ P_i(E,\theta) \ 
\]

(19)

\( v_r \) is nearly constant in our experiment, so (18) may be written as

\[
S(\Theta) = A n_1 n_2 \Delta V v_r BC \sum_i \int \int \int I_i(\theta) \ P_i(E,\theta) \ \frac{v}{\sqrt{E}} \ p(y_1,y_2) dyd^3y_2d^3y_1
\]

(20)

A comparison of (17) and (20) shows that

\[
B = \frac{1}{An_1 n_2 v_r \Delta V} \ 
\]

(21)

At each collision energy, the stagnation pressure of the \( H_2 \) was adjusted to keep the \( H_2 \) flux into the main chamber (measured by the pressure rise when the beam was on) constant, so \( n_2 = n_{H_2} = \frac{1}{V_{H_2}} \). Thus the energy dependent part of \( B \) is \( \frac{v_{H_2}}{v_r} \). The partial total and differential cross sections are related by
The correction factor for comparing partial cross sections derived from (16) at different energies is therefore \( \frac{C v_{H_2}}{v_r} \).

The corrected partial and total cross sections are shown in figure 31. The normalized partial cross sections given by \( \sigma_i = \sigma_i / \sigma \) are shown in figure 32. The total cross section for \( F + p-H_2 \) is indicated by the solid circle in figure 31, and the partial cross sections are listed in table II. The branching ratios for each state relative to \( v = 2 \) are given by \( \sigma_i / \sigma_2 \) and are listed in table III. The trends shown here will be discussed in the next section.

One result worthy of immediate discussion, however, is the much larger \( v = 3' \) partial cross section at 1.84 kcal/mole from \( F + p-H_2 \) than from \( F + n-H_2 \) (see table III). The rotational population of the \( n-H_2 \) beam with \( J > 2 \) is about 5 percent, whereas the \( p-H_2 \) beam is about 20 percent \( J = 2 \). Thus the larger amount of \( v = 3' \) from \( F + p-H_2 \) suggests that it is in fact due to the reaction of ground state \( F \) atoms with rotationally excited \( H_2 \). The results presented in the following chapter on isotope effects substantiate this claim.
Discussion

A. Angular distributions and dynamical resonances

The angular distributions obtained in this study have shown a striking feature not seen in previous experimental work nor in any scattering calculation. This feature, the $v = 3$ forward peak, was observed at every collision energy we studied, even below 1 kcal/mole where the back-scattered product was starting to disappear. The distributions also showed highly state-specific behavior. There was no sign of forward-peaked $v = 2$ product, although this state was sideways-peaked at the highest collision energies.

The first important question to address is whether our unusual angular distributions can be described within the framework of classical mechanics. We can compare our results to angular distributions obtained in classical and quasi-classical trajectory calculations to see if there is any precedent for a forward $v = 3$ peak. The distributions obtained from classical calculations are not divided into product internal states. Thus one expects a state-specific effect to be less noticeable than in our experiment. The summed differential cross sections in figures 18-21 can be directly compared to the angular distributions generated from classical trajectory calculations. The experimental results still show prominent forward peaks, although more scattering occurs in the backward hemisphere because the $v = 2$ state is predominantly backward-scattered. No classical calculation on any model surface for $F + H_2$ has resulted in an angular distribution of this form for
collision energies below 12 kcal/mole. An early calculation by Muckerman showed some forward-scattered product at 2.50 kcal/mole, but this distribution decreased monotonically from 180° and showed no sign of a peak at 0°. A calculation on the same surface at 1.00 kcal/mole showed no scattering for θ < 30°.

The differences between our results and trajectory studies are further emphasized by a comparison with quasi-classical calculations. In this method, the reactants are in an initially well-defined state n with vibrational action \((n + 1/2)\hbar\), and a reactive trajectory is assigned to product vibrational state \(n'\) if its final action is in the range \((n\hbar, (n + 1)\hbar]\). This allows the determination of vibrationally state-resolved differential cross sections which can be more meaningfully compared with the experimental results. The calculations on M5 at 5 kcal/mole collision energy show all the HF vibrational states are dominated by backward-scattering, although a small amount of forward-scattered product occurs for each state. The calculated distribution for \(v = 3\) shows a large peak at 180° and a much smaller peak at 0°. This is in sharp contrast to our \(v = 3\) distributions at considerably lower energies which are dominated by forward-scattering and show no peak at 180°. Unfortunately, quasi-classical angular distributions have not been calculated on surfaces other than M5 so one cannot assess the classical effects of changes in the surface on the state-resolved distributions.

It can be argued that it might be possible to construct a reasonable potential energy surface that can reproduce our results by quasi-classical calculations. After all, up until now there has not
been much incentive to devise a surface that results in substantial forward-scattered product. However, it seems unlikely that such high state-specificity could be achieved in a classical calculation. It would seem especially difficult to obtain more forward scattering in \( v = 3 \) than in the other vibrational states. The high impact parameter collisions necessary for forward scattering result in an effective centrifugal potential in the critical region of the potential energy surface. The \( v = 3 \) product is already 0.5 kcal/mole endothermic, and the centrifugal term plus the \( v = 3 \) adiabatic barrier should inhibit \( v = 3 \) formation from high impact parameter collisions. No such constraints apply to the lower HF vibrational states, as the production is sufficiently exothermic to overcome the possible effects of small exit barriers.

It should be noted that exit barrier effects tend to be de-emphasized in a forward quasi-classical calculation. The exit barrier height relative to the product well is approximately proportional to the final vibrational action of a trajectory. Thus, products formed with final vibrational action \( 3.1\hbar \) are counted as \( v = 3 \), but they can pass virtually unimpeded over an exit barrier that would completely block products with the correct final action \( 3.5\hbar \). The \( v = 3 \) exit barrier is responsible for the delayed onset seen in the quantal calculation of figure 1 in which no \( v = 3 \) product is seen until 0.05 eV above its energetic threshold, indicated by the arrow in the figure. There is no sign of this effect in a forward quasi-classical calculation on M5. Exit barriers are much better accounted for in reverse quasi-classical calculations which start with a well-defined
product vibrational state. Reverse q-c calculations of the reaction probability to form \( \text{H}_2(v = 0) \) from \( \text{HF}(v = 3) \)^{22,68} indeed show a delayed onset very close to the predicted value of 2.4 kcal/mole for the \( v = 3 \) adiabatic barrier height.\(^{33}\) A reverse calculation of the \( \text{H}_2(v = 0) \) angular distribution from \( \text{HF}(v = 3) \) shows much less forward scattering than the \( \text{HF}(v = 3) \) distribution resulting from a forward calculation at the same total energy.\(^44\) Thus a more rigorous quasi-classical treatment, in which all trajectories with final vibrational action outside a narrow range centered at \( 3.5\hbar \) are discarded, should result in a \( v = 3 \) distribution even more back-scattered than in the standard quasi-classical calculations.

It appears that the experimental results cannot easily be rationalized by classical considerations. However, the \( v = 3 \) forward peak is the type of highly state-specific effect that might be expected to result from dynamical resonances. Unfortunately, all the three-dimensional quantal calculations have been performed on M5 and predict that resonance effects will appear in the \( v = 2 \) state rather than in \( v = 3 \).\(^{29,41,42}\) This was explained in the Introduction as resulting from the magnitude of the \( v = 3 \) product adiabatic barrier on M5 which prevents decay of the quasi-bound state to \( \text{HF}(v = 3) \). If our results are due to dynamical resonances, the implication is that the quasi-bound state preferentially decays to form \( \text{HF}(v = 3) \) and the M5 potential energy surface must be modified to mitigate the effect of this barrier.
The $v = 3$ forward scattering is observed over a wide energy range. The three-dimensional quantal calculations show that this is the expected behavior for a dynamical resonance. The range of orbital angular momenta over which a resonance is accessible shifts to progressively higher values of $L$ as the collision energy is raised. To first order, when a collision occurs with orbital angular momentum $L$, the effective centrifugal term displaces the potential energy surface in the vicinity of a resonance and its confining barriers upwards by a constant energy given by $B_L(L + 1)$, where $B$ is an appropriate rotational constant. Pollak has determined the rotational constant for collinear FHH at the M5 $v = 3$ exit barrier to be $3 \text{ cm}^{-1}$. Suppose the true $v = 3$ adiabatic barrier height is $1.0 \text{ kcal/mole}$ above the reactant zero point energy. For a collision with $L = 15h$, the barrier height will be increase by $2.4 \text{ kcal/mole}$ for a total height of $3.4 \text{ kcal/mole}$ relative to $H_2 (v = 0)$. This is the highest collision energy we studied. An effect of similar magnitude is expected in the vicinity of the entrance channel barrier. At this energy $L = 15h$ corresponds to an impact parameter of about $1\text{ Å}$. Thus the centrifugal effects for reasonable values of $L$ are sufficiently large to allow trapping of the quasi-bound state over the energy range we studied.

Although the resonance-enhanced contribution at high $L$ should result in a broader product angular distribution than would occur without a resonance, it does not seem entirely likely that an intense forward peak results simply from collisions at impact parameters near $1 \text{ Å}$. In a classical trajectory study by Blais and Truhlar on $F + D_2$, angular distributions were obtained at fixed values of the impact parameter.
At 6 kcal/mole collision energy, the distributions were backward-peaked at $b = 0.5\text{Å}$ and sideways-peaked near 90° at $b = 1.45\text{Å}$, but no product was observed at $\theta < 45°$ even at the higher impact parameter. However, the forward scattering can be significantly enhanced if the resonance lifetime is a non-negligible fraction of the rotational period of the complex. Assuming a rotational constant of 3 cm$^{-1}$, the rotational period will be $5.5 \times 10^{-13}$ sec for a collision with $L = 10\hbar$. If the lifetime of the complex is 25% of the rotational period, and this is used as the time delay, $\tau$, due to the resonance, then the energy width of the resonance given by $4\hbar/\tau$ is 0.02 eV or 0.4 kcal/mole. This is somewhat broader than the resonances seen in the collinear calculations, which should be expected as the additional bending vibrational degrees of freedom may cause the wells to be shallower and the quasi-bound state lifetime to be shorter. This energy width is comparable to that obtained by Schatz and Kuppermann in a three-dimensional close-coupling calculation for an $L = 0$ resonance in $\text{H} + \text{H}_2$.69

The scattering near $\theta = 0°$ is further enhanced by effects associated with angular momentum conservation. Our kinetic energy analysis reveals that most of the $v = 3$ product is formed in $J \leq 2$ at 1.84 kcal/mole and $J \leq 3$ at the higher energies. This means that for a high orbital angular momentum collision that forms $v = 3$ product, $L$ is largely conserved and appears as $L'$, the product orbital angular momentum. The entire reactive encounter therefore occurs in a single plane perpendicular to $L$. For true long-lived complexes that survive for several rotational periods, the condition $L = L'$ results in a
symmetric angular distribution peaking strongly at 0° and 180°.\textsuperscript{70} This occurs because all orientations of $L$ perpendicular to the reactant relative velocity vector are equally likely. Thus while the scattering in each plane perpendicular to $L$ for a long-lived complex is isotropic, the sum over all scattering planes results in an angular distribution that approaches $(\sin \theta)^{-1}$ in the limit of large $L$. The presence of only a single peak at 0° without a backward peak at 180° in our results indicates the resonance survives a fraction of a rotation at most. This upper bound is consistent with the calculation in the preceding paragraph. Even if the scattering in a single plane is anisotropic, the $(\sin \theta)^{-1}$ form factor due to the symmetry of the angular momentum vector with respect to the relative velocity should still apply to the large $L$ collisions that access the resonance. If the complex survives for a fraction of a rotation before dissociating, the resulting HF product should be preferentially scattered in the range $0° < \theta < 90°$ which will lead to a peak at 0° in the differential cross section. For collisions that do not strictly conserve $L$, the form factor is different and does not provide nearly as much amplification near 0° and 180°.\textsuperscript{70} The HF products formed with $J > 2$ are, for the most part, the result of collisions in which $L$ is not strictly conserved, and the angular distributions for these states might not be expected to be as intense near $\theta = 0°$ as for HF states with $J < 2$. This may explain the abrupt narrowing of the $\nu = 3$ rotational distributions observed near 0°.
The trend in the three F + n-H$_2$ contour maps showing enhanced forward scattering of the v = 3 product as the collision energy is raised is reasonable in light of the above considerations. At higher translational energies the resonance is accessed by higher orbital angular momentum collisions which not only result in a stronger correlation between $L$ and $L'$, but which also result in a quasi-bound state with a shorter rotational period. If the lifetime of the quasi-bound state remains the same, the complex formed at higher $L$ can rotate more before dissociating and increase the amount of HF product scattered into the forward hemisphere. This effect might be countered to some extent by the shorter lifetime of the resonance formed at high $L$ as the repulsive centrifugal potential begins to wash out the adiabatic well supporting the quasi-bound state. At sufficiently high energy, the trend towards increased forward scattering should reverse as the contribution from resonances becomes less important. We do not seem to have reached this point in our experiment.

B. Implications for the potential energy surface.

The discussion so far has shown that the major features of the HF(v = 3) angular distributions can be described in terms of dynamical resonances. However, significant differences remain between our results and the quantal calculations on M5 which are most likely due to deficiencies in the M5 surface, some of which were pointed out in the Introduction. The level of detail obtained in our experimental results is such that further specific changes in the critical region of the surface can be proposed. One modification mentioned previously
is that the \( v = 3 \) adiabatic exit barrier should be reduced so that the low energy resonance can decay to HF\((v = 3)\). Additional support for this, which is independent of the existence of resonances, comes from our low energy experiments. The \( v = 3 \) exit barrier is also responsible for the delayed onset of \( v = 3 \) product seen in the collinear and three-dimensional quantal calculations on M5 in which virtually no \( v = 3 \) product is predicted below 1.2 kcal/mole collision energy. Our results show no sign of this as we observe \( v = 3 \) product at collision energies as low as 0.7 kcal/mole. It is true that the small size of the \( v = 3 \) Newton circle at low collision energies increases our sensitivity for detecting that state in a LAB angular measurement relative to the \( v = 2 \) state, but this is insufficient to compensate for the complete dominance of the \( v = 2 \) product predicted by the calculations at low energies. It should be mentioned that quantal collinear calculations on slightly different potential energy surfaces show markedly different behavior. Connor's calculation on the Muckerman 1 surface, for example, shows no sign of a delayed onset for \( v = 3 \), and it shows a sharp spike in the \( v = 3 \) reaction probability just above the threshold for \( v = 3 \) product. The M1 surface is, in general, inferior to M5 as its exothermicity is too low by 3 kcal/mole, but the point is that the features of M5 that do not agree with our results are certainly not fundamental properties of the F + H\(_2\) system.

The presence of forward scattering at collision energies as low as 0.7 kcal/mole indicates that dynamical resonances are evident at much lower collision energies than occurs in calculations on M5. The calculations predict that the changes in the angular distribution due to
the resonance should appear only at collision energies higher than 2 kcal/mole.\textsuperscript{29,42} This happens because the lowest energy $L = 0$ resonance on M5 occurs at approximately 1.7 kcal/mole above the reactant zero point energy. Suppose, however, that the correct surface has a deeper well than M5 so that the $L = 0$ resonance is below our lowest collision energy.\textsuperscript{71} In this case even at the lowest energy only nonzero collisions could access the resonance resulting in sideways and forward scattering such as we observed. In fact, it is possible for the energy of the collinear quasi-bound state to be below the reactant zero point energy. In this case, the resonance will not appear in a collinear calculation, but it will show up in a three-dimensional calculation.

The $v = 2$ angular distributions also merit some discussion. The sideways-peaked $v = 2$ product at 2.74 and 3.42 kcal/mole is similar to what was seen in the previous crossed molecular beams studies of $F + H_2$.\textsuperscript{45,46} The earlier assignment of the sideways-peaking to resonance effects seems somewhat doubtful in light of the current results. It might seem that the quasi-bound state responsible for the $v = 3$ forward peak should be coupled to some extent with the angular distribution of HF($v = 2$). However, Connor's collinear calculation on M1 shows that the resonance just above the $v = 3$ threshold decays almost entirely to $v = 3$ product; similar structure occurs in the $v = 2$ reaction probability curve but it is less intense by at least a factor of 30. In any case the energy dependence of the $v = 2$ sideways-peaking is so different from the $v = 3$
forward-peaking that it is difficult to imagine that the same quasi-bound state decays competitively to both product states. It is possible that the \( v = 2 \) broadening and sideways-peaking is a classical effect not seen on M5 because the bending force constant near the entrance channel barrier is too high.

C. Integrated cross sections

The integration of our differential cross sections is expected to obliterate most of the effects associated with dynamical resonances. Nonetheless, the ability to obtain relative total and partial cross sections is useful as it should permit more meaningful comparison with a wider range of theoretical studies than is possible with experiments which only yield branching ratios. Our \( F + n\text{-H}_2 \) results show that the total reaction cross section increases with collision energy, although it appears to rise less steeply above 2.74 kcal/mole. This qualitatively agrees with classical and quantal calculations on M5. Each method used to calculate the total cross section gives somewhat different results.\(^{42}\) The smaller slope of the total cross section vs. energy above 2.74 kcal/mole is most evident in the \( J_z \)-conserving quantal calculation,\(^{29,41}\) but, with so many discrepancies between our results and the calculations on M5, it is unclear that our results show this to be a more valid calculation than the others.

The collision energy dependence of the partial and normalized cross sections in figures 31 and 32 and the branching ratios in table III can be summarized as follows. The partial cross section for each product vibrational state increases as the collision energy
is raised. However, the $v = 3/v = 2$ branching ratio decreases whereas the $v = 1/v = 2$ ratio increases with collision energy. The normalized cross section results show the $v = 1$ product rising at the expense of $v = 3$ while the fraction of $v = 2$ product remains relatively constant. The experimental results for the energy dependence of the $v = 3/v = 2$ ratio do not agree with quantal calculations on $M5$. These predict a steadily increasing $v = 3/v = 2$ ratio up to collision energies of 0.5 eV. This discrepancy may be due in part to the high $v = 3$ barrier on $M5$, as the $v = 3$ channel should open up rapidly in the energy range near the barrier. However, it is not clear that even removing the barrier entirely will reverse the trend in the calculated branching ratios because the reaction to form $v = 3$ is endo-thermic by 0.5 kcal/mole. It is possible that the appearance of resonance effects in the $v = 3$ product instead of $v = 2$ is the cause of the difference between our experiment and the calculations.

Our results for the partial cross sections and branching ratios can also be compared to the previous results obtained with chemical laser (CL) and IR chemiluminescence (IC) techniques. However, it should be noted that we can independently vary the reactant translational and rotational energy, whereas in the other studies in which the reactant temperature is varied, translation and rotation are simultaneously affected. Nonetheless, our results are in qualitative agreement with the CL studies and, to a lesser extent, the IC work.

There appears to be considerable variation in the value of the $v = 3/v = 2$ branching ratio for $F + n-H_2$ at 300°K among the IC and CL studies ranging from 0.48$^3$ to 0.63. Our result of 0.68 at
1.84 kcal/mole is close to the high value. Although the temperature corresponding to a mean collision energy of 1.84 kcal/mole is around 600°K, our value is in the right range. It might indeed be expected to be at the high end of the spectrum of values as it is the one experiment where it is guaranteed that no vibrational relaxation of the \( v = 3 \) product can occur.

Our results concerning the translational energy dependence of the \( v = 3/v = 2 \) and \( v = 1/v = 2 \) branching ratios agree with the CL work of Coombe. In an IC study by Perry and a more recent one by Barnes, the \( v = 1/v = 2 \) ratio increased with temperature but the \( v = 3/v = 2 \) ratio remained constant. The reactants are not at thermal equilibrium in their experiment, however, and this may contribute to the discrepancy.

D. Effect of reactant rotation

The contour maps for \( F + n-H_2 \) and \( F + p-H_2 \) at 1.84 kcal/mole in figures 22 and 23 and the LAB angular distributions in figure 8 show that there is considerably less forward peaking of the HF\((v = 3)\) product from H\(_2\)(J = 1) than from H\(_2\)(J = 0). It appears that resonance effects are less pronounced when starting from H\(_2\)(J = 1). This may be an indication of how reactant rotation is coupled to the degrees of freedom of the reaction intermediate. If the H\(_2\) rotational energy goes into overall rotation of the quasi-bound state, a large change in the strength of resonance effects would not be expected. This type of coupling should be most facile for collisions of orbital angular momentum \( L \) such that the energy gap between rotational levels \( L \) and
$L + 1$ of the quasi-bound state is equal to the $H_2$ rotational energy. $H_2(J = 1)$ has 120 cm$^{-1}$ rotational energy, and, assuming the rotational constant of the quasi-bound state to be 3 cm$^{-1}$, this energy matching condition will be satisfied for a collision at $L = 20\ell$. It would seem that a quasi-bound state could not be formed by such a collision at 1.84 kcal/mole as its rotational energy would exceed the translational energy by a factor of two. However, the energy matching condition may not be very strict in practice, as the short lifetime of the quasi-bound state results in an energy width in the range of 10-30 cm$^{-1}$.

Another possibility is that $H_2$ rotation is coupled to bending motion of the FH$_2$ complex. In contrast to coupling with overall rotation, this could result in an overall reduction of resonance effects for several reasons. Ron et al.\textsuperscript{44} have shown that on M5, the $v = 0$ entrance barrier and the $v = 3$ exit barrier coalesce at an F-H-H bending angle of $20.7^\circ$, in which case they cannot possibly support a quasi-bound state. This implies that bending motion near the transition state may lower the probability of forming a quasi-bound state. If a quasi-bound state with bending excitation does form, the additional internal energy might shorten its lifetime. A third consideration is that the $H_2$ rotational energy is, most likely, considerably less than the bending frequency of the quasi-bound state; the bending frequency at the M5 transition state is 450 cm$^{-1}$, for example. A combination of reactant rotation and translation is necessary to produce bending excitation in the quasi-bound state. If a quasi-bound state is formed in which some reactant translation is tied up in its bending motion, less energy
is available for its zero-point stretching modes and overall rotation. This means that such a quasi-bound state can only be accessed by lower collisions than in the case where no bending motion is excited. Any combination of these three effects will result in less forward scattering in the product angular distributions. Our results are consistent with at least some coupling between $H_2$ rotation and bending motion of the reaction intermediate.

Although resonance effects are less evident from $H_2(J = 1)$, the direct reaction appears to be enhanced at 1.84 kcal/mole. The partial cross sections for $v = 3$ and $v = 2$ are slightly higher for $F + n-H_2$ than for $F + p-H_2$ as is the relative total cross section. Classical trajectory calculations on several potential energy surfaces have also predicted that $H_2(J = 1)$ is more reactive than $H_2(J = 0)$ in this energy range. If the $v = 3$ and $v = 3'$ partial cross sections are summed, then the $v = 3/v = 2$ branching ratio is slightly higher for $F + p-H_2$ than for $F + n-H_2$ at the same collision energy. This agrees with previous experimental work in which the two reactions were studied at the same temperature using the IC and CL techniques.

We can also attempt to extract information on the reactivity of $H_2(J \geq 2)$ from our results. The $v = 3'$ partial cross sections for both $F + n-H_2$ and $F + p-H_2$ are about a factor of three smaller than would be expected based on the beam populations with $J \geq 2$, assuming that the variation of the cross section with $J$ is small. The uncertainty in the $v = 3'$ contribution necessary to fit our data is certainly less than a factor of three. It appears our results indicate that the reactivity of $H_2$ drops considerably for $J \geq 2$. This result
has been predicted in several classical trajectory calculations,\textsuperscript{14,15,17} although Polanyi has pointed out that model surfaces with attractive wells in the entrance channel do not show this effect.\textsuperscript{15} However, an experimental measurement of the relative rate constants for F + n-H\textsubscript{2} and F + p-H\textsubscript{2} between 175° and 298°K shows a considerably smaller fall-off of the rate constant with H\textsubscript{2} rotation than indicated by either the calculations or our experiment.\textsuperscript{73} Since a forward v = 3\textsuperscript{\prime} peak would be outside of the effective range of our detector, it is quite possible that our v = 3\textsuperscript{\prime} partial cross sections are incorrect and too low.

E. Reactivity of F(2P\textsubscript{1/2})

The reaction of F(2P\textsubscript{1/2}) with H\textsubscript{2} does not correlate to ground state products,\textsuperscript{74} but semi-classical calculations have predicted a small contribution to reaction via a non-adiabatic transition in the entrance channel.\textsuperscript{75,76} Close-coupling calculations of inelastic F(2P\textsubscript{1/2}) + H\textsubscript{2} scattering have shown that the near resonant process

\[
F(2P_{1/2}) + H_2(J = 0) \rightarrow F(2P_{3/2}) + H_2(J = 2)
\]

is about an order of magnitude more efficient than any other electronic quenching process.\textsuperscript{77,78} This might lead one to propose that if quenching is followed by reaction on the ground state surface with the newly formed H\textsubscript{2}(J = 2), then the reactivity of F(2P\textsubscript{1/2}) should be higher with p-H\textsubscript{2} than with n-H\textsubscript{2} because of the larger J = 0 population in p-H\textsubscript{2}. However, it is difficult to believe that this process can
lead to more reaction than the reaction between $F(^2P_{3/2})$ and $H_2(J = 2)$ already in the beam. Thus the previous assignment of the $v = 3'$ state to rotationally excited $H_2$ is more convincing even if it is slightly less exotic. The result is that our data can be fit without assuming any contribution to the reaction from $F(^2P_{1/2})$. If the reactivity of $H_2(J = 2)$ with $F(^2P_{3/2})$ is similar to that of $H_2(J = 0)$, the contribution from $F(^2P_{1/2})$ must be very small. The $F + n-H_2$ results clearly indicate that $F(^2P_{1/2}) + H_2(J = 1)$ does not produce an appreciable amount of product.
Conclusion

The vibrationally state-resolved differential cross sections for $F + H_2$ presented here represent the most detailed experimental study in reaction dynamics to date. The results, at the very least, provide a database which will greatly aid in the development of a potential energy surface of chemical accuracy for this reaction. More significantly, the explanation of the results in terms of dynamical resonances provides a direct link between the details of the critical region on the potential energy surface and the asymptotic scattering observed in our experiment. Within the resonance framework, the results point to specific modifications to be made to the critical region of the M5 surface. The results of our studies on the $F + HD$ and $F + D_2$ reactions in the following paper will further substantiate the importance of dynamical resonances for this system.
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59. Bulova Electronics Division, Woodside, N. Y.


<table>
<thead>
<tr>
<th>Reaction</th>
<th>H$_2$ source temp (°K)</th>
<th>H$_2$ source pressure (psig)</th>
<th>beam velocity ($\times 10^4$ cm/s)</th>
<th>collision energy (kcal/mole)</th>
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<td>F+p-H$_2$(P)</td>
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<td>119</td>
<td>40</td>
<td>15.45</td>
<td>0.68</td>
<td>0.58</td>
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<tr>
<td>P</td>
<td>167</td>
<td>50</td>
<td>19.67</td>
<td>1.00</td>
<td>1.71</td>
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<tr>
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<td>50</td>
<td>19.67</td>
<td>1.00</td>
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<tr>
<td>P</td>
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<td>22.92</td>
<td>1.30</td>
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<tr>
<td>P</td>
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<td>27.83</td>
<td>1.84</td>
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<tr>
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<td>27.83</td>
<td>1.84</td>
<td>1.00</td>
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<tr>
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<td>95</td>
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<td>2.74</td>
<td>1.03</td>
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<tr>
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<td>110</td>
<td>38.80</td>
<td>3.42</td>
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Table II

Relative cross sections for $F+p\rightarrow H_2$, 1.84 kcal/mole

<table>
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<tr>
<th>$v$</th>
<th>Value</th>
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</thead>
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<tr>
<td>1</td>
<td>36.5</td>
</tr>
<tr>
<td>2</td>
<td>185.1</td>
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<tr>
<td>3</td>
<td>125.2</td>
</tr>
<tr>
<td>3'</td>
<td>8.9</td>
</tr>
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</table>

Table III

$F+H_2$ branching ratios

<table>
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<tr>
<th></th>
<th>$F+p-H_2$ 1.84 kcal/mole</th>
<th>$F+n-H_2$ 1.84 kcal/mole</th>
<th>$F+n-H_2$ 2.74 kcal/mole</th>
<th>$F+n-H_2$ 3.42 kcal/mole</th>
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<tbody>
<tr>
<td>$v=1/v=2$</td>
<td>0.20</td>
<td>0.21</td>
<td>0.23</td>
<td>0.33</td>
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<tr>
<td>$v=3/v=2$</td>
<td>0.68</td>
<td>0.67</td>
<td>0.53</td>
<td>0.48</td>
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<tr>
<td>$v=3'/v=2$</td>
<td>0.048</td>
<td>0.015</td>
<td>0.016</td>
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Figure captions

Fig. 1  Quantal collinear calculation of $F + H_2$ reaction probability on the M5 potential energy surface. $E$ is the total energy and $E_0$ is the translational energy ($E_0 = E - 0.27$ eV, the $H_2$ zero-point energy). The top graph shows the total reaction probability starting from $H_2(v = 0)$, and the bottom graph shows the reaction probability for the $HF(v = 2)$ and $v = 3$ states (ref. 22).

Fig. 2  Contours for the collinear M5 surface in skewed, mass-weighted coordinates, and the hyperspherical coordinates $\pi$ and $\alpha$ (ref. 38).

Fig. 3  Vibrationally adiabatic curves for the collinear M5 surface. $R_0$ corresponds to $H_2(v = 0)$, $P_3$ corresponds to $HF(v = 3)$, etc.

Fig. 4  Top cross-sectional view of the beam sources and collision region. 1) $H_2$ source (70 $\mu$ orifice) 2) coaxial heater cable 3) liquid nitrogen contact 4) 18 mil skimmer 5) supersonic $H_2$ beam 6) $F$ oven 7) $F$ beam 8) velocity selector 9) differential chamber cold shield 10) radiation shield 11) mounting block for velocity selector 12) 150 Hz tuning fork chopper 13) UHV rotatable mass spectrometric detector
Fig. 5 LAB angular distribution for $F + p-H_2$, 1.84 kcal/mole, and Newton diagram. Both the data and calculated LAB distributions are shown (• data, --- total calculated, --- $v = 1$, --- $v = 2$, ----- $v = 3$, --- $v = 3'$).

Fig. 6 $F + n-H_2$ LAB angular distributions at various collision energies.

Fig. 7 $F + p-H_2$ LAB angular distributions at various collision energies. The distributions labelled (N) are for $F + n-H_2$.

Fig. 8 LAB angular distributions for $F + H_2 (J = 0)$ and $J = 1$. The innermost and next smallest Newton circles are for HF($v = 3$) product from $H_2 (J = 0)$ and $J = 1$, respectively.

Fig. 9 Time-of-flight spectra for $F + p-H_2$, 1.84 kcal/mole.

(Δ data, --- total calculated, --- $v = 1$, --- $v = 2$, ----- $v = 3$, --- $v = 3'$). The solid line is not shown when it obscures a vibrational state.

Fig. 10 Time-of-flight spectra for $F + n-H_2$, 1.84 kcal/mole.

Fig. 11 Time-of-flight spectra for $F+H_2$, 2.74 kcal/mole

Fig. 12 Time-of-flight spectra for $F+H_2$, 3.42 kcal/mole
Fig. 13 TOF spectra for F+H₂, 1.84 kcal/mole, at θ = 8°, showing effusive contribution observed close to the F beam. Top graph: solid line is raw data, dotted line is scaled TOF spectrum taken at θ = 4° (see text). Bottom graph shows result of subtracting the effusive background.

Fig. 14 LAB angular distribution for F+n-H₂, 1.84 kcal/mole, showing computer-generated fit to the LAB data (• data, --- total calculated, --- v=1, --- v=2, --- v=3, --- v=3').

Fig. 15 LAB angular distribution for F+n-H₂, 2.74 kcal/mole, showing computer-generated fit to the LAB data.

Fig. 16 LAB angular distribution for F+n-H₂, 3.42 kcal/mole, showing computer-generated fit to the LAB data.

Fig. 17 Energetics of the F+H₂ reaction. All values are in kcal/mole.

Fig. 18 Best fit CM parameters for F+p-H₂, 1.84 kcal/mole.
(--- total (top graph only), --- v=1, --- v=2, --- v=3, --- v=3')

Fig. 19 Best-fit CM parameters for F+n-H₂, 1.84 kcal/mole.
Fig. 20 Best-fit CM parameters for F+n-H₂, 2.74 kcal/mole.

Fig. 21 Best-fit CM parameters for F+n-H₂, 3.42 kcal/mole.

Fig. 22 Center-of-mass velocity flux contour map for F+p-H₂, 1.84 kcal/mole, with three-dimensional perspective.

Fig. 23 Center-of-mass velocity flux contour map for F+n-H₂, 1.84 kcal/mole, with three-dimensional perspective.

Fig. 24 Center-of-mass velocity flux contour map for F+n-H₂, 2.74 kcal/mole, with three-dimensional perspective.

Fig. 25 Center-of-mass velocity flux contour map for F+n-H₂, 3.42 kcal/mole, with three-dimensional perspective.

Fig. 26 Sample rotational distributions for HF product at various CM scattering angles.

Fig. 27 Plots of \( \langle F_J \rangle \) and \( \langle J \rangle \) (see text) for the product vibrational states as a function of CM scattering angle, for F+p-H₂, 1.84 kcal/mole

(--- --- v=1, --- --- v=2, ------- v=3).

Fig. 28 \( \langle F_J \rangle \) and \( \langle J \rangle \) for F+n-H₂, 1.84 kcal/mole.
Fig. 29 $\langle F_J \rangle$ and $\langle J \rangle$ for F+n-H$_2$, 2.74 kcal/mole.

Fig. 30 $\langle F_J \rangle$ and $\langle J \rangle$ for F+n-H$_2$, 3.42 kcal/mole.

Fig. 31 Relative cross sections for F+n-H$_2$ as function of collision energy( ______ total, --- --- -- v=1, ---- v=2, ------ v=3, --- v=3'). The solid circle is the relative total cross section for F+p-H$_2$, 1.84 kcal/mole.

Fig. 32 Normalized cross sections for F+n-H$_2$ as function of collision energy.
Fig. 1
Fig. 2
Fig. 3
F+para-H₂ → HF+H

1.84 kcal/mole
\[ F + H_2 \rightarrow HF + H \]

\[ E = 3.42 \text{ KCAL/MOLE} \]

\[ E = 2.74 \]

\[ E = 1.84 \]

\[ E = 1.00 \]

\[ E = 0.68 \]

\[ H_2 \]

\[ F \]

\[ \text{LAB.SCATT. ANGLE, } \theta \]

\[ N(\theta) \]

Fig. 6
Fig. 7
F + H₂ → HF + H
E = 1.84 KCAL

Fig. 8
F+p-H₂ → HF+H, 1.84 kcal/mole

Fig. 9a
F+p-H$_2$→HF+H, 1.84 kcal/mole

![Graphs showing the change in N(t) with varying temperatures.

Fig. 9b]
$F + p-H_2 \rightarrow HF + H$, 1.84 kcal/mole

$N(t)$ (arb. units)

$t/\mu\text{sec}$

Fig. 9c
F + p - H$_2$ → HF + H, 1.84 kcal/mole

Fig. 9d
F + n-H₂ → HF + H, 1.84 kcal/mole

Fig. 10a
F+n-H₂ → HF+H, 1.84 kcal/mole

Fig. 10b
F+n-H₂ → HF+H, 1.84 kcal/mole

Fig. 10c
F+n-H₂→HF+H, 1.84 kcal/mole

Fig. 10d
F + H₂ → HF + H, 2.74 kcal/mole

Fig. 11a
$F + H_2 \rightarrow HF + H$, 2.74 kcal/mole

Fig. 11b
F + H₂ → HF + H, 2.74 kcal/mole

Fig. 11c
F + H₂ → HF + H, 2.74 kcal/mole

Fig. 11d
F + H₂ → HF + H, 2.74 kcal/mole

Fig. 11e
F+H$_2$ → HF+H, 3.42 kcal/mole

Fig. 12a
F+H₂ → HF+H, 3.42 kcal/mole

Fig. 12b
F + H₂ → HF + H, 3.42 kcal/mole

Fig. 12c
F+H₂→HF+H, 3.42 kcal/mole

Fig. 12d
$F + H_2 \rightarrow HF + H$, 3.42 kcal/mole

Fig. 12e
Fig. 13
F+n-H$_2$→HF+H

1.84 kcal/mole

Fig. 14
F + H₂ → HF + H

2.74 kcal/mole

Fig. 15
F + H₂ → HF + H

3.42 kcal/mole

Signal (Hz)

Fig. 16
$F + H_2(v=0, J=0)$

$\Delta E = 32.07 \pm 0.20$

$HF(v=3)$

$32.53$

$HF(v=2)$

$22.16$

$HF(v=1)$

$11.33$

$HF(v=0)$

$\text{Fig. 17}$
F+p-H$_2$→HF+H, 1.84 kcal/mole

Fig. 18
F+n-H$_2$ → HF+H, 1.84 kcal/mole

Fig. 19
F + H₂ → HF + H, 2.74 kcal/mole

Fig. 20
$F + H_2 \rightarrow HF + H$, 3.42 kcal/mole

Fig. 21
F+p-H$_2$→HF+H, 1.84 kcal/mole

Fig. 22
F+n-H₂→HF+H, 1.84 kcal/mole

Fig. 23
F+n-H₂ → HF+H, 2.74 kcal/mole

Fig. 24
\[ F+n-H_2 \rightarrow HF+H, \ 3.42 \text{ kcal/mole} \]
$F + p - H_2 \rightarrow HF + H$, 1.84 kcal/mole

Fig. 27
F+n-H₂ → HF+H, 1.84 kcal/mole

Fig. 28
F + H₂ → HF + H, 2.74 kcal/mole

Fig. 29
F\( + \text{H}_2 \rightarrow \text{HF} + \text{H} \), 3.42 kcal/mole

Fig. 30
Relative Cross Sections for $F+H_2$
Normalized Cross Sections
for F+H₂

Fig. 32
Chapter II
Molecular Beam Studies of the $F + D_2$ and $F + HD$ Reactions

Introduction

The previous chapter described a high resolution crossed molecular beam investigation of the $F + H_2$ reaction in which center-of-mass angular and kinetic energy distributions were determined for each HF product vibrational state. This paper discusses similar work on the $F + D_2$ and $F + HD$ reactions. The purpose of these studies was to elucidate trends in the series

\[ F + HD \rightarrow HF + D \quad (1) \]
\[ F + H_2 \rightarrow HF + H \quad (2) \]
\[ F + D_2 \rightarrow DF + D \quad (3) \]
\[ F + HD \rightarrow DF + H \quad (4) \]

in order to obtain a global perspective on the chemical dynamics governing this fundamental set of reactions. In particular, we were seeking to reinforce the interpretation of the $F + H_2$ results in terms of dynamical resonances by determining the effect of isotopic substitution on the product angular distributions.

Previous experimental and theoretical investigations have examined several features of these reactions that are sensitive to isotopic substitution. A consistent set of absolute and relative rate constants has been determined in a series of kinetic studies.$^{1-5}$ Product energy distributions have been obtained using chemical laser$^6$ and infrared chemiluminescence$^7,8$ techniques and were also investigated in classical trajectory studies on model potential energy
surfaces. The key experimental findings are as follows. All four reactions produce highly inverted product vibrational distributions. The HF product from reactions (1) and (2) is primarily formed in \( v = 1 - 3 \) with the maximum population in \( v = 2 \), whereas most of the DF population from (3) and (4) is in \( v = 2 - 4 \) with the maximum population in \( v = 3 \). While the DF vibrational distributions from (3) and (4) are similar, the HF (\( v = 3 \)) population from (1) is substantially lower than from (2). Finally, the fraction of available energy in product rotation, \( <f_R> \), decreases progressively from (1) to (4).

Most of the trends in these experimental results are readily explained in terms of the differences in the reaction energetics due to the various zero-point energies and vibrational energy spacings as shown in figure 1, and the results of classical trajectory calculations. The vibrational population distributions are reasonable in light of the similarity in the energetics for producing vibrationally excited HF and DF. The DF (\( v = 4 \)) and DF (\( v = 3 \)) states are at similar energies relative to \( D_2 (v = 0) \) as the HF (\( v = 3 \)) and HF (\( v = 2 \)) states are to \( H_2 (v = 0) \). The reaction to form HF (\( v = 3 \)) from HD is 1.3 kcal/mole endothermic whereas from \( H_2 \) it is only 0.5 kcal/mole endothermic. Thus one would expect HF (\( v = 3 \)) from (1) to be suppressed at thermal energies. Classical trajectory studies have reproduced the trend in product rotational excitation, and this has also been explained using an impulsive model in which the fraction of product repulsion going into rotation is determined by a relation between the product masses. The calculated and experimental
results are in reasonable agreement on $f_v$, the fraction of available energy appearing as product vibration, although there is some disagreement among the experiments and trajectory calculations concerning the relative values of $f_v$ for HF and DF from (1) and (4), respectively. The effect of reactant rotation on the reaction cross section has been studied in several trajectory calculations. The most interesting result, that the HF/DF branching ratio from $F + HD$ depends strongly on HD rotation, has not been experimentally confirmed nor will it be in this paper.

The general agreement between experiment and classical trajectory calculations breaks down when the reactions are examined in greater detail. A substantial conflict occurs in the product angular distributions. Previous molecular beam studies of $F + D_2$ showed predominantly backward-scattered product, whereas the results of the previous chapter showed strong forward peaking of the HF ($v = 3$) product from $F + H_2$. On the other hand, the angular distributions determined from classical trajectory studies are dominated by backward scattering for all four reactions, although they show a slight trend towards increasing sideways scattering from (4) to (1). The question then arises as to whether the differences in the experimental angular distributions are in agreement with the trend expected from quantum mechanical reactive scattering effects.

The results of collinear quantal calculations by Schatz et al. of the reaction probability vs. collision energy are shown in figure 2. The sharp spikes in these curves are associated with dynamical resonances, and the physical origin of the resonances was discussed in the
previous paper. The calculations show significant variations in the strength of the dynamical resonances for reactions (1) to (4). The curves for F + D$_2$ and F + HD → DF + H show broad DF (v = 3) and v = 4 features similar to the v = 2 and v = 3 results from F + H$_2$.

However, the sharp resonance in the HF (v = 2) curve is less evident in the DF (v = 3) curve from F + D$_2$ and has disappeared in the DF (v = 3) curve from F + HD. The most striking result is the F + HD → HF + D calculation. There is a sharp spike in the HF (v = 2) curve near threshold and virtually no other product at higher collision energies up to 0.2 ev. The collinear calculations therefore indicate that reaction (1) is dominated by resonance scattering, and that the relative contribution of resonant to direct scattering progressively decreases from (1) to (4).

The potential energy function is the same for all four reactions, but the kinetic energy terms in the hamiltonian differ for each mass combination. For a collinear reaction, the mass effects are most clearly seen in the skewed, mass-weighted coordinate system which allows the entire reaction to be viewed as the motion of a single particle in a two-dimensional potential. The skew angle between the reactant and product valleys is given by $\alpha = \tan^{-1} \left( \frac{m_B M}{m_A m_C} \right)^{1/2}$ for A + BC → AB + C, where $M = \Sigma m_i$. $\alpha = 37.3^\circ$ for (1), increases progressively from (1) to (4), and is $56.7^\circ$ for (4). The classical effects of $\alpha$ have been known for some time. At small values of $\alpha$, collinear trajectories are less likely to lead to reaction as the
critical region of the skewed surface becomes more reflective. More recently, Babamov and Pollak have independently shown that the vibrationally adiabatic wells and barriers are enhanced at smaller values of $\alpha$, and this leads to more pronounced resonance effects. Thus, while the near absence of direct scattering for $F + HD \rightarrow HF + D$ is somewhat surprising, the general trends in the quantal collinear calculations are reasonable in light of the above considerations.

The extension of the collinear calculations to three dimensions was described in the previous paper. At collision energies above the three-dimensional $J = 0$ resonance, the angular distribution for the product vibrational state(s) resulting from the decay of the resonance should exhibit increased sideways and forward scattering. If the resonance interpretation is correct, then this effect in the angular distributions should be strongest for $F + HD \rightarrow HF + D$ and progressively weaker for reactions (2) - (4). The experimental observation of this trend would therefore lend considerable support to the claim in the previous chapter that dynamical resonances play a significant role in the reaction dynamics of $F + H_2$. The $F + HD$ reaction is especially interesting in this regard, as the HF and DF channels are opposite ends of the 'resonance hierarchy'. Approximate 3-D quantal treatments of $F + HD$ indeed show that the DF product is backward-scattered, whereas the HF product shows strong sideways and, in one calculation, forward scattering.
The comparison between the earlier F + D₂ work and the recent F + H₂ study certainly appears consistent with the quantal predictions. The F + D₂ reaction was therefore re-examined with the current high resolution apparatus in order to better characterize the product distributions. The F + HD work reported here is the first crossed molecular beams study of this reaction.
Experimental

The apparatus and methodology for these studies were identical to the $\text{F} + \text{H}_2$ work described previously. The detection of DF product was considerably easier than HF product as mass 21 was one of the masses with very low background in the detector. The background count rate was less than 5 Hz with the detector closed, and at least some of this was due to field ionization from the 30 kV electrode in our Daly ion counter. There was no contribution from residual rare gas to this mass, and, better still, there was no background problem associated with the F beam as there was when HF was detected, as virtually no conversion of F to DF occurred inside the F source chambers. The problems in detecting HF reactive signal close to the F beam were therefore absent. Thus, the modifications described in the previous paper to lower the mass 20 background were superfluous for the detection of DF.

HO was synthesized in our laboratory by the reaction of $\text{D}_2\text{O}$ with LiAlH$_4$ dissolved in tetrahydrofuran. The HD was compressed into aluminum storage cylinders at pressures as high as 1500 psi. Its purity was checked by photoionization mass spectroscopy and was estimated to be 98%. Before admitting the HD to the beam source, it was passed through a molecular sieve trap immersed in liquid nitrogen in order to remove atmospheric impurities.
Results

Angular distributions of the products from $F + D_2$ and $F + HD$ were taken at several collision energies. The beam conditions for all the scans are displayed in Table I. The DF LAB angular distributions from $F + D_2$ are shown in figures 3-5. $\theta_{CM}$ is the angle between the LAB velocity vector for the F beam and the most probable LAB velocity vector for the center-of-mass. Roughly speaking, LAB angles greater than $\theta_{CM}$ represent backward scattering in the CM frame of reference.

The two lower energy angular distributions in figures 3 and 5 are qualitatively similar. They are both dominated by peaks corresponding to back-scattered $v = 4$ and $v = 3$ product. The signal at 0.79 kcal/mole is considerably lower because this collision energy is close to the entrance channel barrier height of the potential energy surface. The peaks are better resolved in this scan than at 1.82 kcal/mole. This is partly due to the smaller $v = 4$ circle at the lowest energy, but it also indicates that the product scattering in the center-of-mass is more strongly backward-peaked at 0.79 kcal/mole.

The $F + D_2$ angular distribution at 3.00 kcal/mole is quite different from the one at 1.82 kcal/mole. The backward-scattered $v = 4$ and $v = 3$ peaks are less distinct, there is considerably more forward scattering, and there is a small peak at $\theta = 10^\circ$ which appears to correspond to $v = 4$ product scattered near $\theta = 0^\circ$ in the CM. This peak is reminiscent of the forward $v = 3$ peak observed in the $F + H_2$ angular scans. At this energy, the entire $v = 3$ circle is within
range of the rotating detector. We looked for forward scattered $v = 3$ product on the other side of the F beam but did not find any.

The F + HD angular distributions are shown in figures 6-8. It is clear that the HF and DF product angular distributions are not at all alike. The DF angular distributions at all three energies consist mainly of backward-scattered $v = 4$ and $v = 3$ product. They resemble the lower energy F + D$_2$ angular scans. The outstanding feature in the HF angular distributions at 1.98 and 1.35 kcal/mole is a peak corresponding to forward scattered $v = 3$ product. The back-scattered $v = 3$ and $v = 2$ peaks seen in F + H$_2$ are nearly absent here, although both scans show a small bump that drops off near the backward edge of the $v = 3$ circle which probably is from a small amount of sideways or backward scattered $v = 3$. The scan at 1.35 kcal/mole is barely above the threshold for $v = 3$ formation, and the scan at 0.8 kcal/mole is well below it. The disappearance of the peak at 0.8 kcal/mole shows that it is indeed due to HF ($v = 3$). The signal attributable to HF ($v = 2$) is rather featureless at all three energies. The $v = 2$ circle is too large for any forward-peaked product to be within range of the detector. However, no signal was seen on the other side of the F beam at any energy. There is a rise in the signal at 0.82 kcal/mole at LAB angles $< 15^\circ$ which appears at 1.35 kcal/mole as a plateau between the forward $v = 3$ peak and the F beam. It is apparent to a lesser extent at 1.98 kcal/mole. We are uncertain if this is reactive signal due, possibly, to sideways scattered $v = 2$, or if it is an artifact resulting from being too close to the F beam. The two lower energy angular
distributions show that the DF signal drops off considerably below 1.35 kcal/mole.

Time-of-flight measurements were taken for F + D₂ at 1.82 and 3.32 kcal/mole, and for F + HD at 1.98 kcal/mole. Attempts to obtain TOF spectra of the HF product from F + HD anywhere but the forward peak were unsuccessful due to the low signal-to-noise ratio, so we were unable to construct a contour map for the HF channel. 16 TOF spectra were taken at each F + D₂ energy, and 12 DF spectra were taken for F + HD. The complete set of TOF spectra is displaced in figures 9, 10, and 11, along with the assignments to product vibrational states obtained by the CM → LAB analysis.

The TOF spectra for F + D₂ at 1.82 kcal/mole show well-resolved \( v = 3 \) and \( v = 4 \) peaks at most angles. Two \( v = 4 \) peaks are observed at angles that cut across the \( v = 4 \) circle, and these peaks merge at angles near \( \Theta = 42^\circ \) (fig. 9b) which is nearly tangent to the circle. At this angle three peaks, corresponding to \( v = 2 \), \( v = 3 \) and \( v = 4 \), are observed, and the \( v = 2 \) peak becomes more evident at larger angles. The \( v = 1 \) state appears at \( \Theta = 66^\circ \) (fig. 9c) as a fast shoulder at the base of the \( v = 2 \) curve. The curves labelled \( v = 4' \) will be discussed in the Analysis section.

The resolution of the product vibrational states in the TOF spectra for F + D₂ at 3.32 kcal/mole is considerably worse than at 1.82 kcal/mole as the \( v = 4 \) circle is larger. Nonetheless one can partially resolve vibrational states at all angles. The TOF spectrum at \( \Theta = 10^\circ \) (fig. 10a) shows that most of the forward peak in the angular scan is
due to $v = 4$. The $v = 1$ state is evident at more angles than at 1.82 kcal/mole. The DF spectra from F + HD show resolution comparable to the low energy F + D$_2$ time-of-flight. The resolution is somewhat worse because the $v = 4$ and $v = 3$ circles are closer.
Analysis

The determination of the center-of-mass angular and kinetic energy distributions was done with the same forward convolution procedure as was used for $\text{F} + \text{H}_2$. Again, it was necessary to account for the reactant rotational populations in estimating the total available energy for the calculations. This is more of a problem for $\text{D}_2$ than for HD. Rotational relaxation of HD in a supersonic beam is relatively efficient as the HD can undergo $\Delta J = 1$ transitions which are more facile than the $\Delta J = 2$ transitions required for the homonuclear species, and can result in virtually complete relaxation to $J = 0$. In addition, the displacement between the center-of-mass and the center-of-charge results in a more anisotropic interaction potential for HD which promotes rotational relaxation. From Pollard's photoelectron data\textsuperscript{28} we estimate that greater than 90% of the HD is in $J = 0$ with nearly all the rest in $J = 1$. The exothermicity of 32.9 kcal/mole was used as the total available energy for $\text{F} + \text{HD} \rightarrow \text{DF} + \text{H}$. The $\text{D}_2$ can, at best, have a $J = 1:J = 2$ ratio of 1:2, and the restriction to even $\Delta J$ transitions results in less rotational cooling in the expansion. The $\text{D}_2$ populations for the room temperature beam are estimated to be 40% $J = 0$, 30% $J = 1$, 25% $J = 2$, and most of the rest in $J = 3$.

For $\text{F} + \text{D}_2$ at 1.82 kcal/mole, the $J = 1$ population was explicitly accounted for by adding 0.2 kcal/mole to the exothermicity in figure 1 resulting in a value of 32.1 kcal/mole for the total available energy. This gave acceptable fits to all the time-of-flight spectra except at $\Theta = 42^\circ$ and $\Theta = 46^\circ$(fig. 9b). These LAB angles are nearly tangent.
to the DF \((v = 4)\) Newton circle and sample strongly back-scattered \(v = 4\) product. The faster part of the \(v = 4\) peaks at these angles could be fit by assuming a small contribution from the reaction of F with \(D_2\) \((J = 2)\), and this contribution is labelled \(v = 4'\). The analogous TOF spectra for the F+HD reaction, at \(\Theta = 40^\circ\) and \(\Theta = 42^\circ\) (fig. 11b), required no additional state to fit the data. As the HD beam has virtually no rotational excitation, this further supports the claim that the \(v = 4'\) product from F + D\(_2\) and the \(v = 3'\) product from F + H\(_2\) is from rotationally excited reactants rather than from spin-orbit excited F\((2^P_{1/2})\).

The F + D\(_2\) data at 3.32 kcal/mole could not be fit near the forward or the backward edge of the \(v = 4\) circle with a total available energy of 32.1 kcal/mole. The D\(_2\) \((J = 2)\) population in the high temperature beam might be as high as twice the population in the room temperature beam because of the higher stagnation temperature and the lower inverse Knudsen number\(^{28}\) for the expansion. The \(J = 2\) rotational energy was included in the total available energy at this energy as the resolution was too poor to justify as separate \(v = 4'\) state.

The computer-generated fits to the F + D\(_2\) LAB angular distributions are shown in figures 3 and 4. The best fit CM parameters for the three systems are graphically displayed in figures 12-14. As in the previous chapter, the coupled energy and angular distribution is given by
\[ P_i(E, \theta) = N_i I_i(\theta) \left( 1 - \frac{E}{E_m^i} \right)^{a_i(\theta)} \left( \frac{E}{E_m^i} \right)^{b_i(\theta)} \]

with

\[ b_i(\theta) = a_i(\theta) \left( \frac{E_p^i(\theta)}{1 - E_p^i(\theta)} \right). \]

\( I_i(\theta) \) is the integrated intensity of vibrational state \( i \) at \( \theta \), \( E_p^i(\theta) \) is the maximum in the recoil energy distributions, and \( a_i(\theta) \) determines the width of the recoil energy distribution. \( E_m^i \) is the maximum recoil energy for state \( i \), and was chosen for \( v = 4' \) assuming \( D_2(J=2) \) rotational excitation.

The center-of-mass velocity flux contour maps are displayed in figures 15-17. The \( F + HD \) map shows that all four observed DF vibrational states are backward-peaked. The \( F + D_2 \) contour map at 1.82 kcal/mole shows the \( v = 3, 2, \) and \( 1 \) states peaking at or near 180°. The \( v = 4 \) state shows a broad sideways peak centered around 130°, and it extends further into the forward hemisphere than the \( v = 4 \) state from \( F + HD \). The \( v = 4' \) state is scattered entirely into the backward hemisphere.

The \( F + D_2 \) contour map at 3.32 kcal/mole shows that the \( v = 3, 2, \) and \( 1 \) distributions have broadened considerably relative to 1.82 kcal/mole. The \( v = 3 \) distribution is sideways-peaked at this energy. The \( v = 4 \) distribution has changed the most dramatically, however. It shows a forward peak at \( \theta = 0° \), a sharp dip near 20°, and is almost isotropic for \( \theta > 30° \).
The F + D₂ relative partial cross sections for each vibrational state, \( \sigma_i \), the relative total cross sections \( \sigma = \Sigma \sigma_i \), and the normalized partial cross sections \( \sigma'_i = \sigma_i / \sigma \) at the two collision energies are shown in figures 18 and 19. The branching ratios derived from this work for F + D₂ and F + HD as well as some of the results from earlier chemiluminescence work are tabulated in Table II. The \( v = 4' \) and \( v = 4 \) contributions have been summed in the cross section graphs and the branching ratio table. The \( v = 4' \) partial cross section is about 10% of that for \( v = 4 \) at 1.82 kcal/mole. Any statement concerning the reactivity of D₂ (J = 2) relative to lower rotational states cannot be very definitive due to the ambiguity in distinguishing the \( v = 4 \) and \( v = 4' \) contributions to the TOF spectra. The \( v = 4' \) partial cross section represents a lower bound since the data was fit with as little \( v = 4' \) as possible.

Table II shows that the \( v = 4/v = 3 \) and \( v = 2/v = 3 \) ratios for F + D₂ at 1.82 kcal/mole and F + HD \( \rightarrow \) DF + H are somewhat lower than the chemiluminescence values. However, there is not much difference between the F+D₂ and F+HD ratios, and the \( v = 4/v = 3 \) ratio is higher than the \( v = 2/v = 3 \) ratio for both reactions. These comparisons agree with the chemiluminescence results. The variation of the partial cross sections and branching ratios with collision energy for F + D₂ is similar to that seen for F + H₂ in the previous chapter. All the partial cross sections increase with collision energy, but the \( v = 4/v = 3 \) ratio decreases whereas the \( v = 2/v = 3 \) ratio increases. For
F + H₂ the \( v = 3/v = 2 \) ratio decreased and the \( v = 1/v = 3 \) ratio increased as the collision energy was raised. Figure 19 shows that the \( v = 2 \) and \( v = 1 \) products increase at the expense of \( v = 3 \) and \( v = 4 \) as the energy is raised. The trend in the kinetic energy dependence of the \( v = 2/v = 3 \) ratio agrees with the temperature-dependent chemiluminescence results but not with an earlier chemical laser study which showed a significant drop in this ratio with increasing temperature. A decrease in the \( v = 4/v = 3 \) ratio does not occur in the chemiluminescence study at the higher temperature.
Discussion

The results presented here and in the previous paper show that there are marked differences in the product angular distributions within the set of isotopic reactions (1) to (4). While classical trajectory studies predict a tendency for the angular distributions to become progressively less strongly backward-peaked for the sequence (4) - (1), the extent of the variation observed here seems well beyond what would be expected from a classical calculation on any reasonable potential energy surface. The observed trends in the angular distributions are, on the other hand, readily explained in terms of various combinations of direct reactive scattering, which can be reproduced in classical trajectory calculations, and dynamical resonance phenomena.

Reaction (4), \( F + HD \rightarrow DF + H \), behaves the most classically of the four reactions. The contour map at 1.98 kcal/mole shows all the product vibrational states to be backward-peaked. This is the expected result for a potential energy surface favoring collinear approach of the reactants. The rapid fall-off in the product yield as the collision energy is lowered from 1.35 to 0.82 kcal/mole is consistent with the behavior expected for a direct reaction at collision energies near the mechanical barrier for reaction, although it is possible that the contribution from tunneling is important at the lowest energy.

One difference between reaction (4) and the \( F + H_2 \) and \( D_2 \) reactions is that the quantal collinear calculations on M5 do not predict nearly as much of a delayed onset for DF \((v = 4)\) product from (4) as they do
for DF (v = 4) from F + D₂ and HF (v = 3) from F + H₂. The delayed onset refers to the energy difference between where a product vibrational state is energetically accessible and where it first appears in the scattering calculation, and it is thought to be due to a v = 4 or, for F + H₂, a v = 3 adiabatic barrier in the product valley of the potential energy surface. The 1 kcal/mole additional exothermicity of reaction (4) relative to (3) reduces the effect of the v = 4 barrier for (4). The observation of v = 4 product from (4) at 0.82 kcal/mole therefore does not contradict the results of the M5 calculations. However, the F + D₂ scan at 0.78 kcal/mole also shows v = 4 product even though the M5 collinear calculations predict a delayed onset of > 1 kcal/mole. This again indicates that the M5 surface should be modified so as to reduce the v = 4 exit barrier. For F + H₂, it was suggested in the previous chapter that lowering the v = 3 exit barrier would cause resonance effects to appear in the v = 3 product rather than v = 2 as predicted on M5. Similarly, the DF (v = 4) product might be expected to be influenced by resonances rather than v = 3 once the v = 4 barrier is lowered.

Our results for F + D₂ indeed suggest that this is occurring. The contour map at 1.82 kcal/mole shows that the v = 4 product, while predominantly scattered into the backward hemisphere, shows sideways peaking. At the higher energy, the angular distributions for all four observed vibrational states are broader, which is the expected classical result as more non-collinear collisions contribute to the
reaction. However, the $v = 4$ distribution is considerably different from the others as it is the only one showing a forward peak. This resembles the behavior calculated for $F + H_2$ on M5 in which backward-scattering occurred at 2 kcal/mole collision energy, and, when the collision energy was raised to 3 kcal/mole, the resonance-enhanced contribution to reaction at higher impact parameters resulted in a state-selective broadening of HF ($v = 2$). The experimental results, on the other hand, showed forward-peaked $v = 3$ from $F + H_2$ at collision energies as low as 0.7 kcal/mole. This was attributed to the $\text{L} = 0$ resonance being below the lowest collision energy. If the $v = 4$ scattering for $F + D_2$ is interpreted in terms of dynamical resonances, the results suggest that the $\text{L} = 0$ resonance energy is higher than for $F + H_2$. Thus, if the resonance is being accessed at all at 1.82 kcal/mole, it is probably being formed only by low impact parameter collisions which result in a primarily back-scattered angular distribution. The forward scattering occurs at the higher energy where the resonance can be accessed only by higher $\text{L}$ collisions.

The quantal collinear calculations predict the lowest resonance for $F + D_2$ to be higher relative to the reactant zero point energy than for $F + H_2$ as the adiabatic curve supporting the quasi-bound state is considerably shallower,\textsuperscript{21,29} so our experimental results for $F + H_2$ and $F + D_2$ are consistent with this. The calculations also predict a shorter lifetime for the $F + D_2$ resonance, and the larger skew angle for $F + D_2$ should result in more direct vs. resonant scattering than for $F + H_2$. The contour map for $F + D_2$
at 3 kcal/mole shows far less forward scattering than any of the
F + H₂ contour maps, and this is consistent with the implications of
the collinear results.

While the results for reactions (2) - (4) can be explained in terms
of dynamical resonances and the 'resonance hierarchy' inferred from
the collinear calculations, the F + D₂ and F + HD → DF + H results
considered by themselves might not be considered sufficient proof for
the existence of resonance effects. The stronger backward-scattering
for DF (v = 4) from F + HD compared to F + D₂ at 1.82 kcal/mole might
be due to the greater contribution of small impact parameter collisions
to F + HD because the center-of mass of HD is closer to the D atom.
The forward-scattering of v = 4 at 3.32 kcal/mole is accompanied by
sideways-peaked v = 3 product, so the broadening of the angular dis-
tribution is not nearly as state-specific as for F + H₂. The state-
ment that no reasonable potential energy surface could reproduce the
high energy F + D₂ angular distribution in a classical trajectory
calculation cannot be made with as much confidence as for F + H₂.

The results for F + HD → HF + D, on the other hand, almost force
one to think in terms of dynamical resonances. The most prominent
feature in these angular distributions is a forward-scattered v = 3
peak even at a collision energy just above the v = 3 threshold. This
bears very little resemblance to angular distributions derived from
classical trajectory studies. The collinear quantal calculation on M5
predicts a strong, low energy resonance leading to v = 2 and very little direct scattering. The extension to three dimensions would lead one to expect extensive forward or sideways scattering in the angular distribution reflecting the dominant contribution from high impact parameter collisions at energies above the L = 0 resonance. This is just what we see in our angular distributions, although, as with F + H₂, HF (v = 3) is the observed product of the resonance rather than v = 2.

The collinear resonance for F + HD → HF + D on M5 is only about 0.2 kcal/mole above the reactant zero-point energy and is about 1 kcal/mole below the HF(v = 3) threshold. The bending zero point energy for FHD on M5 is around 1 kcal/mole, so the L = 0 resonance energy in three dimensions should be quite close to the v = 3 threshold which in turn, is close to the collision energy of 1.35 kcal/mole in one of the experiments. The forward peak observed at this energy indicates that the true L = 0 resonance energy should be lower than is predicted on the M5 surface, as was the case with F + H₂. The L = 0 resonance energy could be lowered by reducing the bending zero-point energy or by increasing the depth of the adiabatic well. This last step is likely to lower the collinear resonance below the reactant zero-point energy, in which case it will not show up in a collinear calculation.

The extent of the correspondence between the collinear calculation and the angular distributions for (1) is somewhat exaggerated by the reaction kinematics. The nearly total absence of direct reaction in
the collinear calculation is largely due to the small skew angle, and the suppression of direct scattering should be less for non-collinear collisions. Indeed, the IR chemiluminescence studies shown that $v = 2$ was the dominant product for this reaction. We cannot calculate branching ratios due to the lack of TOF data, but our angular scans are not as inconsistent with this result as it might seem at first glance. The intensity transformation from CM flux to LAB number density is proportional to $v/u^2$, where $v$ is the LAB velocity and $u$ is the CM velocity for the detected product. The $v = 2$ circle is much larger than the $v = 3$ circle for this reaction at 1.98 and 1.35 kcal/mole, and the $u^{-2}$ term reduces the $v = 2/v = 3$ LAB intensity by a factor of 16 at 1.98 kcal/mole and 70 at 1.35 kcal/mole. Thus the CM $v = 2$ flux is far higher than it appears in the angular distributions. The form of the $v = 2$ CM angular distribution is open to speculation. The LAB angular distributions suggest it is quite spread out rather than strongly backward-peaked. It was mentioned previously that forward-peaked $v = 2$ product would be outside the angular range of our detector. The possibility that the $v = 2$ product is strongly influenced by resonances cannot be excluded. In any case, while it may not be true that resonance scattering dominates the entire angular distribution as implied by the collinear calculation, it does appear that the $v = 3$ scattering is dominated by resonance effects to a much greater extent than in F + H$_2$. 
Conclusion

The variation in the angular distributions for the isotopic set of F + H$_2$ reactions is far greater than predicted by classical calculations. It is, however, quite consistent with the resonance hierarchy predicted in quantal reactive scattering calculations. This reinforces the importance of dynamical resonances for these reactions, and supports the claim that state-resolved differential cross sections are the best way to observe resonances in reactive scattering. The effects from resonances appear to be very strong for F + HD $\rightarrow$ HF (v = 3) + D, progressively weaker for F + H$_2$ $\rightarrow$ HF (v = 3) + H and F + D$_2$ $\rightarrow$ DF (v = 4) + D, and do not show up at all in F + HD $\rightarrow$ DF + H at the energies studied here. The changes in the critical region of the M5 surface suggested in the F + H$_2$ studies appear even more reasonable in light of the results presented here.
Chapter II References


18. Figure 1, previous chapter.


Table I
D\textsubscript{2}, HD source conditions for the angular scans

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Source temp(°K)</th>
<th>Source pressure (psig)</th>
<th>beam velocity (10^4) cm/s</th>
<th>collision energy (kcal/mole)</th>
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<tbody>
<tr>
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<td>104</td>
<td>45</td>
<td>11.1</td>
<td>0.79</td>
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<tr>
<td>F+D\textsubscript{2}</td>
<td>307</td>
<td>80</td>
<td>19.6</td>
<td>1.82</td>
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<tr>
<td>F+D\textsubscript{2}</td>
<td>579</td>
<td>110</td>
<td>27.6</td>
<td>3.32</td>
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<tr>
<td>F+HD</td>
<td>111</td>
<td>45</td>
<td>13.9</td>
<td>0.82</td>
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<tr>
<td>F+HD</td>
<td>185</td>
<td>55</td>
<td>18.4</td>
<td>1.35</td>
</tr>
<tr>
<td>F+HD</td>
<td>307</td>
<td>80</td>
<td>23.7</td>
<td>1.98</td>
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Table II
DF product branching ratios for F+D\textsubscript{2} and F+HD

<table>
<thead>
<tr>
<th></th>
<th>F+D\textsubscript{2}</th>
<th>F+D\textsubscript{2}</th>
<th>F+HD</th>
<th>F+D\textsubscript{2}</th>
<th>F+HD</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.82</td>
<td>3.32</td>
<td>1.98</td>
<td>(ref.8)</td>
<td>(ref.8)</td>
</tr>
<tr>
<td>(v=1/v=3)</td>
<td>0.02</td>
<td>0.19</td>
<td>0.02</td>
<td>0.15</td>
<td>0.18</td>
</tr>
<tr>
<td>(v=2/v=3)</td>
<td>0.44</td>
<td>0.67</td>
<td>0.40</td>
<td>0.52</td>
<td>0.54</td>
</tr>
<tr>
<td>(v=4/v=3)</td>
<td>0.49</td>
<td>0.41</td>
<td>0.48</td>
<td>0.59</td>
<td>0.61</td>
</tr>
</tbody>
</table>
Figure captions

Fig. 1  Energetics of the F + H₂, F + D₂, and F + HD reactions. All values are in kcal/mole. H₂, D₂, and HD are in their lowest internal states (v = 0, J = 0).

Fig. 2  Quantal collinear calculation of the reaction probability vs. energy on M5 for F + D₂, F + HD (ref. 17).

Fig. 3  LAB angular distribution for F + D₂, 1.82 kcal/mole, showing computer-generated fit (● data, ——— total calculated, ——— v = 1, ——— v = 2, ——— v = 3, ——— v = 4, ——— v = 4').

Fig. 4  LAB angular distribution for F + D₂, 3.32 kcal/mole, showing computer-generated fit (no v = 4' state here).

Fig. 5  LAB angular distribution for F + D₂, 0.79 kcal/mole.

Fig. 6  LAB angular distribution for F + HD, 1.98 kcal/mole (● HF product, △ DF product). The Newton circles corresponding to HF and DF product are drawn with the same texture as the lines in the angular distributions. The HF(v = 3) and v = 2 circles are shown, as are the v = 4, 3, and 2 circles for DF.

Fig. 7  LAB angular distributions for F + HD, 1.35 kcal/mole.
Fig. 8 LAB angular distributions for F + HD, 0.82 kcal/mole. No HF(v = 3) circle appears as this state is energetically inaccessible.

Fig. 9 Time-of-flight spectra for F + D₂, 1.82 kcal/mole (△ data, ——— total calculated, ——— v = 1, ——— v = 2, ——— v = 3, —— v = 4, ——— v = 4'). Solid line not shown when it obscures a vibrational state.

Fig. 10 Time-of-flight spectra for F + D₂, 3.32 kcal/mole.

Fig. 11 Time-of-flight spectra for F + HD, 1.98 kcal/mole.

Fig. 12 Best-fit CM parameters for F + D₂, 1.82 kcal/mole (—— total (top graph only), ——— v = 1, ——— v = 2, ——— v = 3, —— v = 4, ——— v = 4').

Fig. 13 Best-fit CM parameters for F + D₂, 3.32 kcal/mole.

Fig. 14 Best-fit CM parameters for F + HD, 1.98 kcal/mole.

Fig. 15 Center-of-mass velocity flux contour map for F + D₂, 1.82 kcal/mole.
Fig. 16  Center-of-mass velocity flux contour map for $F + D_2$, 3.32 kcal/mole.

Fig. 17  Center-of-mass velocity flux contour map for $F + HD$, 1.98 kcal/mole.

Fig. 18  Relative total and partial cross sections for $F + D_2$
(— total, — — — $v = 1$, — — — $v = 2$,
 — — — $v = 3$, — — — $v = 4$ (4' added at 1.82 kcal/mole)).

Fig. 19  Normalized cross sections for $F + D_2$. 

Fig. 1
Fig. 2
F + D₂, 1.82 kcal/mole

Fig. 3
Fig. 4

F+D₂, 3.32 kcal/mole

Signal(Hz)

θcm

θ

V_F

V_D₂

XBL 841-98
\[ F + D_2 \rightarrow DF + D \]

\[ E = 0.79 \text{ KGal} \]

\[ 5 \times 10^4 \text{ CM/S} \]

Fig. 5
F+HD
1.98 kcal/mole

Fig. 6
Fig. 7

F+HD

1.35 kcal/mole

\[
\Theta_{\text{cm}}
\]

Signal(Hz)

\[
\begin{align*}
&0 \quad 5 \quad 10 \quad 15 \quad 20 \\
&0 \quad 20 \quad 40 \quad 60 \quad 80
\end{align*}
\]

\[
V_{\text{F}}
\]

\[
V_{\text{HD}}
\]

\[
XBL\ 841-97
\]
F+HD
0.82 kcal/mole

Fig. 8
F+D₂ → DF+D, 1.82 kcal/mole

Fig. 9a
F\(+\)D$_2$\(\rightarrow\)DF\(+\)D, 1.82 kcal/mole

![Graph showing the relationship between time and N(t) for various angles.](image-url)
F + D₂ → DF + D, 1.82 kcal/mole

Fig. 9c
F + D₂ → DF + D, 3.32 kcal/mole

Fig. 10a
F + D₂ → DF + D, 3.32 kcal/mole

Fig. 10b
F + D$_2$ $\rightarrow$ DF + D, 3.32 kcal/mole

Fig. 10c
$F + HD \rightarrow DF + H$, 1.98 kcal/mole

Fig. 11a
F+HD → DF+H, 1.98 kcal/mole

Fig. 11b
F + D$_2$ → DF + D, 1.82 kcal/mole

Fig. 12
F+D\textsubscript{2} - DF+D, 3.32 kcal/mole

Fig. 13
F+HD → DF+H, 1.98 kcal/mole

Fig. 14
$F + D_2 \rightarrow DF + D, \ 1.82 \ \text{kcal/mole}$

Fig. 15
F + D$_2$ → DF + D, 3.32 kcal/mole

Fig. 16
F + HD → DF + H, 1.98 kcal/mole

Fig. 17
Relative Cross Sections for F+D$_2$
Normalized Cross Sections for $F + D_2$
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