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Reaction Dynamics of Some Small Systems
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University — Université

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Degree for which thesis was presented — Grade pour lequel cette thèse fut présentée

Ph.D.

Year this degree conferred — Année d'obtention de ce grade

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REACTION DYNAMICS OF SOME SMALL SYSTEMS
CONTAINING POTENTIAL ENERGY WELLS

by

© David James Donaldson, BSc.

A thesis submitted to the Faculty of
Graduate Studies in partial fulfilment
of the requirements for the degree of
Doctor of Philosophy

Department of Chemistry

Carleton University
Ottawa, Ontario
November, 1983

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"REACTION DYNAMICS OF SOME SMALL SYSTEMS
CONTAINING POTENTIAL ENERGY WELLS"

submitted by David James Donaldson in partial
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ABSTRACT

The arrested relaxation infrared chemiluminescence technique for the study of energy disposal in atom/molecule reactions has been extended to allow studies of atom/radical reactions. The radicals are produced chemically in a previous reaction. The technique is described and the results of studies on the systems

discussed. These systems have in common the presence of deep potential energy wells accessible to ground state reactants.

Infrared emission was observed from both vibrationally excited HF ($v' \leq 10$) and CO ($v' \leq 5$) in the F/HCO reaction. Both molecules displayed monotonically decreasing vibrational populations with increasing v -level. That of HF is found to be statistical. The CO is found to be less vibrationally excited than would be expected on this basis. It is therefore concluded that a greater than statistical amount of reaction energy is released as relative translation.

It is demonstrated that the HF vibrational distribution from the reaction

is cold (non-inverted). The HF vibrational inversion observed in the F/NH₃ system is due to the reaction of F-atoms with NH₂. This is

demonstrated clearly both by experiment and by a numerical model of the current apparatus. This model gives an estimate of the vibrational distribution of HF from the radical reaction.

Emission from vibrationally excited CO($v' \leq 14$) is observed in the system O/F/C₂H₄. This is attributed to the reaction of O-atoms with vinyl radicals, formed in the F/C₂H₄ reaction. The measured vibrational distribution of the CO decreases monotonically with v -level, but is considerably more excited than that predicted on statistical grounds. Based on the maximum CO vibrational level observed, the other product must be CH₃. It is concluded that a less than statistical amount of the reaction energy is partitioned into the CH₃ product of the reaction.

Ab-initio calculations are reported on the $^1A'$ and $^3A''$ potential energy surfaces of the O/H₂ system in the configuration O-H-H. These surfaces were constructed using the MRD-CI method to calculate points and the RMCS fitting procedure to generate smooth and continuous surfaces. The crossings between these surfaces are described in detail. The lowest energy crossings are seen to occur at an O-H-H angle of 120° in a region very close to the triplet barrier at this angle. They occur at an energy about 15 kcal/mol above that of the ground state reactants. This is slightly above the lowest energy barrier to the ground state reaction, which is predicted to lie 13.2 kcal/mol above reactants, at an O-H-H angle of 180°. The implications of these findings with respect to the kinetics of the ground state reaction are discussed.

ACKNOWLEDGMENTS

I would like to express my sincere appreciation to the many people who have helped to bring this work into being.

First, I am greatly indebted to Dr. J. J. Sloan, of the National Research Council and Prof. J. S. Wright, of Carleton University, for their patient instruction, encouragement and support during the course of my studies with them. I am also grateful to Prof. J. D. Goddard, of Guelph University, for his collaboration on some of the problems discussed herein and for allowing me to quote some as yet unpublished results. Thanks are also due to Messrs. J. Vandenhoff and P. L'Abbe, for their excellent glassblowing services, Mr. J. Parsons, for technical assistance and to Ms. M. Stock, for her careful typing of this thesis.

To the various people who have been associated with the experimental and theoretical groups, I am very grateful for many stimulating discussions and helpful favours. These people include: N. Adamson, P. Aker, V. Barclay, P. Deidrich, R. Edmonds, L. Pankratz, D. Lee, J. J. A. O'Brian, S. Ransome, A. Stolow and P. Vasu. To D. G. Watson and R. J. Williams, I am especially grateful in this regard, for their companionship and moral support through various crises.

Finally, to my family and friends, who have provided so much over the years, I am forever thankful.

PREFACE

The study of reaction dynamics has, as its ultimate goal, the complete understanding of chemical reactions on a microscopic level. It is thus concerned with determining answers to the following questions: From a given set of reactant quantum states, what corresponding states are populated in the products? How do the various features of the potential energy surface(s) for the reaction influence its outcome? In what way is the outcome changed if the reactant quantum states are changed and which reactant degrees of freedom (translation, vibration etc.) have the most influence in this regard?

The nature of these questions has made the field a very fruitful area for the synthesis of theoretical and experimental studies. Because the events of interest are simple - usually single collisions between small species - the quantum mechanical calculation of the potential energy surfaces of interest becomes feasible, if not always practical. Trajectory studies performed using these potential energy surfaces, or reasonable approximations to them, can give great insight into the detailed events leading to the (experimentally observed) final product quantum state distributions. In addition, changing the initial conditions (i.e. reactant states, relative velocities, etc.) in the trajectory calculation and changing the features of the potential energy surface under study yield insight into which factors have influence over the outcome of a reactive encounter.

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In an ideal experiment, one would be able to both specify the initial conditions of a reaction (reactant quantum states, relative velocities and orientations) and detect the same qualities in the reaction products. Because of the very low pressures required to maintain single collision conditions, however, this is a very difficult goal to attain. In general, it is possible to either specify fairly completely the initial conditions pertaining to the reactants, or to resolve the final product state distributions. In the former case, a crossed molecular beams machine can be used, in conjunction with laser excitation of the molecular beams, to prepare reagents in certain well defined states having a narrow range of relative velocities. The angular and velocity distributions of the products are generally measured in these experiments, the product densities being too low for state resolution. In order to fully state-resolve the products of a reaction, it is usually necessary to use higher pressures than are appropriate for a molecular beams apparatus. The product states are then detected by observation of the spontaneous emission of the internally excited product molecules (chemiluminescence), transient absorption measurements, or by laser-induced fluorescence techniques.

The work presented in this thesis is concerned with the dynamics of small systems in which there is a potential energy well accessible to the reactants. It is divided into two sections, corresponding to experimental and theoretical studies of such systems. In Section A, the experimentally measured energy disposal in the products of a series of atom/radical reactions is reported. These

measurements were made using a modified low pressure infrared chemi-luminescence apparatus. Chapter A.1 describes the technique and the apparatus used in this work. Chapters A.2-A.4 report the results obtained in this manner for the HF and CO energy distributions in the reactions:

These reactions all have deep potential energy wells, corresponding to bound intermediates, accessible to the reagents. However, they give rise to very different patterns of energy disposal in their products. These results and their interpretation are discussed fully in the individual chapters.

Section B of this thesis presents the results of an ab-initio theoretical study of the system O/H₂. In this system, there is a deep potential well corresponding to ground state H₂O which correlates to the first excited state of the O-atom, O(¹D). The presence of this well causes the singlet potential surface containing it to drop below that of the triplet surface connecting ground state reactants and products. The singlet and triplet surfaces were calculated using ab-initio methods and the crossings between them examined in detail. The methods used in the calculation are described in Chapter B.1. The results and their implications with respect to the kinetics of the ground state reaction are discussed in Chapter B.2.

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SECTION A: Infrared Chemiluminescence Studies of
Energy Disposal in Atom/Radical Reactions

Chapter A.1: General Introduction to Section A

A.1.1 Infrared Chemiluminescence

Chemiluminescence is defined to be the emission of photons from excited internal states of molecules formed in a chemical reaction. The infrared chemiluminescence technique is a method whereby the vibrational (and often rotational) state distributions of the product molecules of a chemical reaction are measured directly via this emission.

There are two variants of this technique in current use. In both, the reagents mix diffusively in the gas phase and the infrared emission from the reaction products is measured spectroscopically. The reagent flows are varied until no change in the measured distributions results from a further reduction in reagent concentrations. At this stage, the relaxation of the initially formed populations by the reagent molecules is considered to have been eliminated.

The first variant, the "arrested relaxation" method (1,2), maintains a very low ($< 10^{-3}$ Torr) pressure in the reaction zone through the use of fast pumping. The reagents diffuse into this zone from uncollimated beam sources. Because of the low pressure in the reaction zone, the product molecules suffer very few deactivating collisions with the reagent species in that zone. The relaxation of internal excitation in the product molecules is thus "arrested", due to the very low density of possible collision partners. The measured intensity of fluorescence from the individual rovibrational states of these molecules can then be related directly (via the transition probabilities for spontaneous emission) to the

populations in these states initially formed by the reaction.

The second variant, the "measured relaxation" method (1,2) operates at higher pressures than the first. A very fast flow (ca. 100 m/sec) is established in a long tube in which the total pressure is about 1-3 Torr. Most of this pressure is due to an inert carrier gas, such as He or Ar. The reagents are introduced into this flow and mix diffusively as they are swept along by the carrier gas. The emission from products is measured at a series of ports along the length of the tube (corresponding to different times in the reaction). The product energy distributions measured in this way are extrapolated back to zero time, to obtain the initial distributions. This method is also used with only one observation port (3) situated as close as possible to the point of mixing of the reagents.

The present work represents an extension of the arrested relaxation infrared chemiluminescence method to study the energy disposal in the reactions of atoms with radicals. A reagent inlet device was developed which allowed the radical reagent to be prepared chemically, via the reaction of a molecular precursor with an F-atom. This device is described in detail in the next section. The radicals produced in this fashion then reacted with a second (in some cases different) atomic reagent, introduced separately. The infrared emission from the products of this second, radical, reaction was collected and the energy distributions in those products thus determined.

The reagent radicals studied in this work were produced by the reaction of an F-atom with a polyatomic hydride molecule. These reactions, producing HF and a radical product, have been the object of much study (4,5). The method offers several advantages. The reactions of F-atoms with hydrogen-containing species are generally very fast and quite exoergic (5). The product HF is often formed with a large amount of internal excitation (4,5); inverted vibrational distributions of that product are quite common. Finally, HF has a large transition probability for spontaneous emission (5), hence its vibrational fluorescence is readily detected.

This means of generating reagent radicals in situ by means of a prior chemical reaction was pioneered by Polanyi (6,7) in studies involving reactions of vibrationally excited molecules. It has since been developed extensively in this laboratory (8-12); the present work represents the most recent of these developments.

Using this technique, the energy disposal in the reactions of F-atoms with C_2H_3 (8), OH (10,13) and HNF (9) has been previously measured.

A.1.2

GENERAL EXPERIMENTAL DESCRIPTION

The purpose of this section is to describe, in general terms, the methods by which the experiments were done. Specific details peculiar to any one system, or set of experiments, are given in the experimental section of the chapter concerned with that system. In this section is given a description of the apparatus used, details of the reagents and flow measurements and a description of how the experimental data were gathered and analysed.

a) Description of apparatus

The experiments were carried out in modified low pressure, arrested relaxation infrared chemiluminescence apparatus, which has been extensively used to obtain the initial energy distributions for various atom/molecule reactions⁽¹⁴⁻¹⁹⁾. The apparatus was modified to permit studies of atom/radical reactions. In the studies to be reported here, the radicals were generated by a reaction in which an H-atom is abstracted from a molecular species by an F-atom. The radicals thus generated subsequently reacted with a second atom and the energy distribution in the products of this second reaction was measured. In this manner, energy distributions have been obtained for the systems: F/HNF⁽⁹⁾, F/OH^(10,13), F/NH₂⁽²⁰⁾, F/HCO⁽²⁰⁾, F/C₂H₃⁽⁸⁾, O/C₂H₃⁽²⁰⁾ and F/HS⁽²¹⁾.

The apparatus consists of a reagent inlet assembly, in which the radicals are prepared chemically, a reaction/observation chamber and a high-speed pumping system. It is shown schematically in Figure A.1.1. The three components will be discussed individually.

Figure A.1.1

Schematic diagram of the Reagent Inlet Assembly as mounted in the low pressure apparatus. The range of injector motion is indicated by the arrows.

The reagent inlet, shown in detail in Figure A.1.2, consists of three concentric quartz tubes, coated with teflon (for details of this procedure, see Appendix 1). The innermost of the three, the injector, is used to inject the molecular reagent into the system. It is 4 mm in diameter and, for the experiments reported here, terminated in one of two fashions. For the earlier experiments, the end of the tube was closed and between 6 and 8 circular holes of 1 mm diameter were drilled in a radial pattern about 1-2 mm from the bottom. This caused difficulties in some of the experiments, particularly those involving NH_3 . Solid reaction products formed at the injection holes, making the injection of molecules non-uniform and, in some cases, almost completely blocking the holes. This problem was exacerbated by the tendency of the teflon coating to flake off upon repeated use of the injector, also blocking the holes to some extent. For these reasons, the later experiments used an injector with an open end, which had a small, circular teflon "deflector plate" suspended about 2-3 mm below it. This alleviated both of the above problems and ensured a uniform flow of molecular reagent. The latter arrangement is the one illustrated in the Figure.

The injector was mounted in a fitting which allowed the location of its lower tip (and thus the injection point) to be adjusted vertically within a range of about 5 cm. This fitting consisted of a threaded teflon cylinder (4.2 cm. ϕ .d.) which screwed into an outer cylindrical teflon support. The latter rested on the top of the quartz tube labelled Tube 2, in Figure A.1.1. A 2.4 cm diameter brass rod was

Figure A.1.2

Detail of the Reagent Inlet Assembly, shown to scale. The injector is shown partially withdrawn.

mounted inside the inner teflon cylinder and extended downwards, passing through tube 2 as well. The brass rod had a 6 mm. diameter hole drilled on its central axis, allowing the injector to pass through it. The injector was sealed in by means of an O-ring at the top of the brass rod; two O-ring seals between this rod and tube 2 maintained a vacuum seal while allowing vertical motion of the injector.

The outer two tubes, of diameters 2.5 and 4.6 cm. respectively, were used, for the most part, to supply atoms to the system. A vacuum seal was maintained between them by means of a cylindrical brass fitting through which tube 2 passed. The lower end of this fitting had two O-rings sealing it to tube 1; tube 2 was sealed to the fitting by a third O-ring at the top of the fitting.

The atomic reagents were generated from molecular precursor gases in a 2450 MHz microwave discharge (Raytheon) operating at power levels between 40 and 100 W. The precursor gases flowed into the tubes through quartz sidearms, on which were mounted microwave cavities of the Evenson type, which coupled the input power into the flowing gas and caused dissociation of the molecular precursor. It was found that if the visible part of the plasma induced by the microwave discharge was allowed to extend out of the sidearm and into tube 2, (close to the injector tube on the axis of Tube 2) the injector temperature rapidly rose to about 250°C. Care was thus taken to ensure that the plasma stayed within the sidearm. This was accomplished by moving the discharge cavity back along the sidearm and reducing the power supplied to it. In this way room temperature operation was maintained in the

vertical portions of all tubes.

The three-tube arrangement was an extension of a previous design which included on the moveable injector and Tube 2. Addition of a third, outer, tube allowed radicals which were generated in an F-atom reaction in tube 2 (eg. $F + C_2H_4 \rightarrow C_2H_3 + HF$) to then react with a second, different atom, brought to the reaction zone by tube 1 (eg. $C_2H_3 + O \rightarrow CO + CH_3$). Using a configuration in which the injector was withdrawn inside tube 2, sufficient quantities of the radical reagent could be generated from even slower precursor reactions. }

The reaction/observation chamber, illustrated in Figure A.1.3, consisted of a 25 cm. internal diameter, 30 cm. high stainless steel cylinder. First-surface gold coated concave mirrors mounted to the front and rear walls of the chamber provided a Welsh-type⁽²²⁾ multipass optical collection system. This improved the light collection efficiency by a factor of 50-100 over that involving a single flat mirror mounted on the rear wall of the chamber⁽²³⁾.

A cylindrical liquid nitrogen reservoir was mounted to the underside of the lid of the chamber; the reagent inlet assembly was mounted through a hole in this lid. Suspended vertically from the cold reservoir were a series of copper vanes, which surrounded the observation zone defined by the multipass optics. These vanes formed a radial chevron baffle which is optically dense in the horizontal direction, but provides little obstruction to pumping in the vertical direction. This pattern maximizes the trapping and hence deactivation of any vibrationally excited product molecules diffusing out of the observation region. The cooled vanes also served to lower the pressure in the chamber by

Figure A.1.3

Schematic diagram of the low pressure apparatus with the reagent inlet mounted. The liquid nitrogen reservoir (dotted area), mirrors (shaded-in) and cryobaffles (dashed lines) are shown.

CRYOBAFFLE

DIFFUSION PUMP

cryopumping all gases which condense at 77 K.

The chamber was evacuated through a 30 cm diameter gate valve, then through a 38 cm diameter cryobaffle, also maintained at 77 K by the circulation of liquid nitrogen. This cryobaffle was especially designed for the current apparatus, to provide a high throughput at the expense of some backstreaming. Using this cryobaffle, about 2/3 of the rated pumping speed of the diffusion pump was obtained at the gate valve. A Varian VHS 400 (8000 L/s) 16 inch diameter diffusion pump, backed by a 50 cfm Welch mechanical pump were used to evacuate the system. The base pressure in the reaction/observation chamber was typically 10^{-5} - 10^{-6} Torr (measured behind the cold vanes with a Varian 855-A cold cathode ionization gauge).

b) Reagents

Fluorine atoms were generated in a discharge of SF_6 (Matheson, Union Carbide) or of CF_4 (Matheson); because of the air impurity in the latter, however, it was not used in the studies involving CO emission. Oxygen atoms were formed by discharging molecular oxygen (Matheson). All of these gases were metered directly from the gas cylinders, without further purification. Ethene (Matheson) was used both directly from the lecture bottle and after passing through a molecular sieve trap (Linde 5A) kept at -80°C by a methanol-dry ice slurry. No difference in the results was observed between the two cases. Ammonia and ammonia (d-3) (Matheson and MSD Isotopes, 99 atom % D) were also used with no further purification. Hydrogen and Deuterium (Matheson) were used both directly and, in the case of H_2 , after flowing through a molecular sieve trap as for ethene; again there was no difference observed in the results.

(24)
Formaldehyde was prepared by the method of Spence and Wild, from paraformaldehyde ($(\text{H}_2\text{CO})_3$) (Fisher Scientific, purified grade) and was distilled from a trap at -80°C to one at -196°C before use. On occasion, it was stored for some time at -80°C before use. When this was done, the trap containing the formaldehyde was subjected to pumping for about 15 minutes prior to the formaldehyde's being used. This removed any H_2 impurity which may have been present. There was no difference observed in the results between the samples stored at the two different temperatures.

c) Flow measurements

The flows of reagent gases were measured and controlled in two ways. For most of the experiments, Matheson Tri-Flat mass flowmeters were used, in conjunction with pressure measurements, to measure the gas flow rate. Although this did not regulate the flow, it was found that fairly stable flows could be established and maintained for the length of time necessary to collect data. The absolute error in the flows measured in this manner is estimated to be on the order of 10-20%. For most of the experiments, however, the absolute flow rates were not important; what was important was that they remained constant throughout the data-collection period. This condition was met by careful monitoring of the flow meter readings over the course of an experiment; if they changed more than 2-5% the run was aborted and restarted when the flows became stable.

The second method used to monitor the flows was a four-channel commercial flow control system (Matheson Flow Controller, Model 8249).

This system was only used for the experiments in which it was crucial that the flows remain absolutely steady, at well-known values. As it happened, this was only the case for one set of experiments, involving the F/NH_3 system.

d) Data acquisition

Infrared emission from vibrationally-excited species was collected by the multipass optical arrangement, described above. The radiation thus collected was coupled out of the low-pressure apparatus and into the detection system by a 2 inch diameter CaF_2 lens (f/1). The detection system was a Nicolet 7199 Fourier Transform Infrared (FTIR) spectrometer, consisting of a Michaelson interferometer, an infrared detector and associated optics, electronics for data acquisition and a Nicolet 1180 computer. The data acquisition electronics consisted of high- and low-pass electronic filters, two gain amplifiers, an analog to digital converter and an isolated output amplifier.

The subject of FTIR spectroscopy and its application to chemical problems has been amply reviewed,^(25, 26) and will not be covered here. The specifics of the detection system employed in the present work have been described in detail by Watson⁽²³⁾ and will not be repeated.

Two infrared detectors were used in the experiments to be reported here: an InSb detector (Judson Infrared), cooled to 77 K and a HgCdTe detector, peaking at about 6 μm (Santa Barbara Research Corp.), also cooled to 77 K. The InSb detector was used for the bulk

of the experiments, except those for the O/C_2H_3 system. For the latter case, it was necessary to extend the detection sensitivity to longer wavelengths than those accessible to the InSb detector; the HgCdTe detector was quite adequate for this.

A typical experiment consisted of co-adding 100 interferograms, collected under conditions of stable reagent flows and constant background temperature. As the signal-to-noise ratio increases as $\sqrt{N}$, where N is the number of interferograms co-added⁽²⁶⁾, this number provided a reasonable balance between time spent collecting data (and thus stability of flows, etc.) and optimal signal intensity. The actual collection time was dependent on the resolution of the experiment; for a resolution of 0.48 cm^{-1} , one hundred interferograms typically took ten minutes of collection time.

During data collection, a software routine checked each newly-collected interferogram against the sum of all those collected previously. If the maximum in the digitized zero-path-difference (ZPD) fringes did not match, to within one point, with the maximum of those already co-added, it was rejected. As the ZPD contains all the lowest frequency information (corresponding to background temperature, etc) this procedure ensured that only interferograms collected under identical conditions were allowed to be included in the signal averaging.

When the requisite number of interferograms had been collected (under the lowest flow conditions up to 1000 were co-added), the co-added result was stored on disk, to await processing.

e) Data Analysis

All data analysis was performed using routines (both supplied by Nicolet and user-written) resident in the Nicolet 1180 computer. This allowed all data to be treated in an identical manner, with a minimum of human intervention.

There is a greater intensity of radiation due to the room temperature optics impinging on the detector than there is from the reaction vessel. This background emission gives rise to a curved baseline in the resulting spectra. To eliminate this baseline curvature, the ZPD fringes in the interferograms were zeroed before the Fourier transformation was done. Because the ZPD fringes occur at short times in the interferogram, they correspond to information in the resulting spectrum which varies slowly with frequency, such as baseline curvature. Removing them prior to the transform thus gave rise to a flat baseline; however it also removed all phase information inherent in the ZPD. This necessitated the use of a power transform in the Fourier transformation of the interferograms. This, in turn, caused all excursions from the baseline of the spectrum (whether signal or noise) to be positive.

The interferograms were transformed into the frequency domain by a Fourier transformation, using the Cooley-Tukey Fast Fourier transform algorithm⁽²⁷⁾. The interferograms were apodized using a Happ-Genzel function before transformation.

Following the Fourier transformation, the spectra were corrected for the frequency response of the detector. This was

done by dividing each spectrum by a detector response characteristic, obtained in the following way: Two measurements were made, at two widely different temperatures, of the spectrum of a calibrated commercial blackbody source (Infrared Industries). Each of these spectra contained a room temperature component, due to emission from the optics of the interferometer. By subtracting the colder from the hotter spectrum, this contribution from the room temperature surroundings was eliminated. The same two temperatures were used to calculate "true" blackbody spectra corresponding to those temperatures, using Planck's function. These calculated blackbody spectra were then subtracted, in the same way as the measured ones. The ratio of the measured difference spectrum (with absorption peaks removed) to the calculated difference spectrum then gave the detector response as a function of frequency.

Because of the software problems with the computer, this procedure was not possible in the case of high resolution (0.06 cm^{-1}) spectra. These were only of interest in the case of CO however. The maximum frequency range of observed emission from this molecule was of the order of 500 cm^{-1} ; both detectors varied in response less than 10% over this region. It is thus felt that the derived populations are good to within the quoted error estimates (vide infra).

The relative populations of individual ro-vibrational states of the molecule of interest were then calculated. First, all emission lines in the corrected spectrum were assigned, using transition frequencies calculated from the energies given by a Dunham⁽²⁸⁾ expansion. The latter involved seventeen terms in the

case of HF and ten in the case of CO. The molecular constants used to calculate the energies were those given in Huber and Herzberg (29). Because the instrumental resolution was in all cases less than the Doppler width of the emission lines (ca. $4 \times 10^{-3} \text{ cm}^{-1}$) it is the former which determines the linewidths in the observed spectrum. Due to this, the emission intensities could be related directly (i.e. without having to integrate over the lineshape) to populations via the relation:

$$I_{v'',J''}^{v',J'} = P(v',J') \times A_{v'',J''}^{v',J'}$$

where I is the intensity of the observed emission line, P is the population of the emitting state and A is the Einstein transition probability for spontaneous emission, all for the transition $(v'',J'' \leftarrow v',J')$.

The transition probabilities, required for the extraction of the relative populations from the intensities, were calculated for HF from the rotationless transition probabilities of Sileo and Cool (30) and the vibration-rotation interaction factors of Herman *et al.* (31)

For CO, the experimentally determined rotationless transition probabilities for the $0 \leftarrow 1$ and $1 \leftarrow 2$ vibrational transitions (32) were used to normalize the values determined theoretically by Lightman and Fisher (33) for the $\Delta v = 1$ and $\Delta v = 2$ transitions. Vibration-rotation interaction factors were calculated using the molecular constants given in Huber and Herzberg (29) and the dipole moment expansion (up to fourth order) of Bouanich and Brodbeck (34).

In this way, the relative population of each emitting ro-vibrational state was calculated from the measured spectrum. In addition, the total intensity of these emitting states, corresponding to the total population of excited species observed was calculated. This number is strongly dependent on the conditions in effect (i.e. detector alignment, multipass mirror adjustment, etc) for any given experiment. However, it is of great significance and enormous interpretive value in comparing data taken on the same day (i.e., with the same apparatus configuration). This fact will be made obvious in a later chapter.

The last stage in the data processing was the calculation of the vibrational distributions. This was done by summing over the rotational populations in each vibrational state and normalizing the result such that $\sum_{v'} P_{v'} = 1.0$, where $P_{v'}$ is the population in level v' . Overlaps between two emitting lines were treated by zeroing the populations in the offending states and interpolating between the next higher and lower J-state populations in the particular vibrational manifold using a third order natural cubic spline.

The relative vibrational populations so derived are believed to be accurate in most cases to within $\pm 2\%$ for HF and $\pm 3\%$ for CO. This is the error in precision; it is believed that there are no systematic errors introduced in the analysis procedure as outlined above. The relative total populations are somewhat less well determined; an error of ca. $\pm 10\%$ on these is felt justified. This is because these are very sensitive to small changes in reagent

flows (smaller than those required to cause the data to be rejected in the collection routine). Because the flows could (and did) vary up to about 5% over any given run, the reproducibility of the relative total populations was of the order of 10%. In some cases in which a spectrum showed a poor signal-to-noise ratio ($S/N \leq 4$), the estimated errors on the distributions and relative total populations are greater than those given above. In these cases, the estimated errors are given in the text describing the particular result.

Chapter A.2: The Reaction $F + HCO \rightarrow HF + CO$

A.2.1 INTRODUCTION

The results to be presented in this chapter have been published, in preliminary form, in reference **11**.

The formyl radical, HCO is believed to be an important intermediate in hydrocarbon flames^(35,36) and in interstellar space⁽³⁷⁾. It is also of interest as it is a primary photoproduct of formaldehyde photolysis^(38,39) at energies greater than 32250 cm^{-1} ⁽³⁸⁾:

The spectroscopy of this radical in its ground state has been studied by many methods; both the electronic⁽⁴⁰⁾ and infrared⁽⁴¹⁾ spectra have been recorded. In addition, ESR, LMR and microwave spectra have been reported; Vasudev and Zare⁽⁴²⁾ give a brief summary of spectroscopic work through 1981. This work has provided information on the structure and molecular constants of the ground state $\dot{\text{X}}(^2\text{A}')$ radical.

The equilibrium geometry deduced from the results of ⁽⁴⁰⁾ is: $r(\text{CH}) = 1.125 \text{ \AA}$, $r(\text{CO}) = 1.175 \text{ \AA}$, $\theta(\text{HCO}) = 124.95^\circ$. For comparison, that of ground state formaldehyde is ⁽⁴³⁾: $r(\text{CH}) = 1.102 \text{ \AA}$, $r(\text{CO}) = 1.210 \text{ \AA}$, $\theta(\text{HCH}) = 121.1^\circ$ ($\therefore \theta(\text{HCO}) = 119.4$). Herzberg,⁽⁴³⁾ gives the bond strength of the H-C bond as being between 24.0 and 35.5 kcal/mol, whereas that of formaldehyde is between 69.6 and 82.1 kcal/mol. More recent measurements indicate a value of about 15 kcal/mol.^(44,45) for the H-CO bond.

The very low bond energy is indicative of the types of reaction entered into by this radical. These involve abstraction of the hydrogen atom, leaving the stable molecule CO. Kinetic measurements have been made on the reactions of HCO with O_2 ⁽⁴⁶⁻⁴⁸⁾, NO^(46,48), HCO⁽⁴⁷⁾, H⁽⁴⁷⁾, O⁽⁴⁴⁾ and Br⁽⁴⁹⁾. These reactions are all fast, with room temperature rate constants ranging from 4.5×10^{-12} cc/molec/sec for reaction with O_2 ⁽⁴⁶⁻⁴⁸⁾, to gas kinetic (ca. 1×10^{-10} cc/molec/sec) for the atomic^(44,47,49) and disproportionation⁽⁴⁷⁾ reactions. A trajectory study has also been made of the H + HCO reaction⁽⁵⁰⁾ yielding a total rate constant (ca. 2.6×10^{-10} cc/molec/sec) and predicting the product energy distributions. No kinetic measurements have yet been reported for the F/HCO system, but the reaction, giving HF and CO, is expected, based on the above discussion, to be very fast.

Apart from the preliminary report of this work⁽¹¹⁾, no previous studies of the dynamics of the reaction of F-atoms with formyl radicals have been published. These are expected, however, to be influenced strongly by the presence of a deep potential energy minimum, corresponding to the bound molecule FHC0. Previous experience in this laboratory with other atom/radical systems^(8-10,13) has shown that when such a potential energy minimum is present, a randomization of the reaction energy is often the result, the products being formed with near-statistical energy distributions.

Dynamical studies have been made on two closely-related systems, however. The reaction of ground state oxygen atoms with fluoromethylene: $O(^3P) + CHF \rightarrow HF + CO$ has been reported by Lin

and co-workers ⁽⁵¹⁾. Although the reactants do not correlate directly to ground state products (spin is not conserved), both products were observed in several vibrational levels of the ground electronic state. It was concluded that the reaction proceeded via a long-lived HFCO complex, which started on a triplet potential energy surface, decayed to a singlet state by intersystem crossing, then decomposed to products. The authors of ⁽⁵⁰⁾ also reported that the H₂ and CO energy distributions from the reaction:

were influenced by the presence of the H₂CO potential well, though only a few of the reactive trajectories passed through the minimum of that well (corresponding to the equilibrium H₂CO geometry).

In both of the above cases, the product vibrational distributions were monotonically-decreasing functions of v-level, suggesting their origin in the decomposition of a long-lived complex. Somewhat different results were obtained from an earlier, flash-photolysis experiment on HFCO ⁽⁵²⁾. In this experiment, infrared laser action was observed from a small number of HF (v' = 1,2) J-levels after a photolysis pulse at $\lambda > 1650 \text{ \AA}$. No higher v-levels of HF were seen; no emission was seen at all from CO in excited vibrational states. The authors determined, by scavenging experiments, that the atomic photodissociation channel:

was occurring concurrently with the molecular photoelimination channel,

which produces HF and CO directly. Although those authors did not investigate the excitation wavelength dependence of this result, it is known that for formaldehyde, the atomic photodissociation channel becomes increasingly important at wavelengths less than 310 nm (38).

The reaction

is known to give an inverted vibrational distribution (53); this secondary reaction could well have been responsible for the population inversion and laser action observed in (52).

The present results arose out of an attempt to investigate the dynamics of:

It has been reported (44,54) that highly vibrationally-excited OH ($v' \leq 10$) is formed in this reaction. For the present experiments, the reaction of F-atoms with formaldehyde was used as the source of HCO radicals. No emission was seen from vibrationally excited OH in the preliminary experiments. If this reaction is indeed the source of the vibrationally-excited OH reported in (44,54) and the rate constant is gas kinetic, then emission from the excited OH would have been seen in the present apparatus. On this basis, it seems unlikely that reaction [5] could be responsible for the results reported in (44,54).

Under conditions such that the radical concentration was high, infrared emission was seen from CO and from HF ro-vibrational levels energetically inaccessible to the reaction of F-atoms with formaldehyde. This emission was seen when there was no O₂ (and thus no O-atoms) present in the system. This emission was thus believed to originate in the reaction:

A.2.2 EXPERIMENTAL

Two different reagent inlet assembly configurations were used in these experiments. In the first (configuration A), the bottom of the inner tube (tube 2) was even with the bottom of the outer, (tube 1) and the injector, in its lowest position, extended 3 cm below both. The second configuration, (B), had tube 2 ending about 2.5 cm within tube 1. The injector, at its lowest position, was even with, or ca. 0.5 cm below, the bottom of tube 1. (Two different injector lengths were used for these experiments). These are shown schematically in figure A.2.1.

Formaldehyde was produced from its trimer, paraformaldehyde, by the method of Spence and Wild (24). It was distilled trap-to-trap, under vacuum, from -80°C to -196°C and stored either at -196°C or -80°C until used. No difference in the results was obtained if the formaldehyde was stored at the higher temperature. It was metered into the injector from a trap kept at the temperature corresponding

Figure A.2.1.

Schematic diagrams of reagent-inlet assemblies A and B, as described in the text.

A

B

to the desired vapour pressure through a Matheson tri-flat gas flow-meter. Most experiments were done with the trap at -80°C ; for some higher flow studies, however, the trap was kept at -60°C . These temperatures were maintained by using slush baths: dry ice/methanol for -80°C and liquid nitrogen/octane for the higher temperature.

Fluorine atoms were generated in a microwave discharge of SF_6 (Matheson). CF_4 was not used for these experiments, as it was found previously that the small air impurity in commercial CF_4 could give rise to CO emission under certain circumstances. This may be the result of the reaction ⁽⁵⁵⁾ :

but the point was not pursued.

The experiments were carried out using the InSb detector. The resolution used for all but one of the experiments was 0.48 cm^{-1} ; the remaining experiment was done using 0.06 cm^{-1} resolution.

A.2.3. RESULTS AND DISCUSSION

(a) $F + H_2CO$

The dynamics of the reaction

have been studied previously^(53,55-58). The reaction populates HF vib-rotational levels up to the thermochemical limit; the vibrational distribution is strongly inverted, peaking in $v' = 3$. Table A-I gives the vibrational distributions of HF obtained in two different experiments, both done under conditions such that the contributions to the observed distribution from relaxation and secondary reaction were felt to be negligible. Also shown are the distributions given in references 53, 57 and 58, for comparison. Figures A.2.2 and A.2.3 show respectively, the vibrational and rotational distributions for run 13/29, given in the table.

Because of the low flows used to obtain the data in Table A-I, the signal-to-noise ratio was low. Therefore the distributions shown have estimated errors of $\pm 5\%$ on each v -level. They are in qualitative agreement with those reported by Macdonald and Sloan⁽⁵³⁾ and Holmes and Setser⁽⁴⁾, though somewhat less vibrationally excited than those of the latter. The rotational distributions shown in figure A.2.3 do not appear to have a sizable 300K Boltzmann contribution to them. It is thus suggested that, within the limits imposed by the signal-to-noise, the "initial" energy distributions

Table A-I

Vibrational distributions of HF from F + H₂CO

RUN #	SF ₆ ^{a,b}	H ₂ CO ^a	I.P. ^c	P(v'=1)	P(v'=2)	P(v'=3)	P(v'=4)	Ref.
8/34	1.0	0.5	-2.8	0.18	0.24	0.36	0.22	present
13/29	1.3	0.67	-3.0	0.22	0.25	0.33	0.20	"
13/30	1.8	0.67	-0.5	0.16	0.30	0.35	0.19	"
				0.21	0.29	0.33	0.17	53
				0.13	0.26	0.38	0.23	4
				0.09	0.21	0.46	0.23	58

a) Flows in micromoles/sec

b) Discharge in Tubes 1 and 2

c) Injector position in cm. Negative values indicate distance outside outer tubes.

Figure A.2.2.

HF vibrational distribution from $F+H_2CO \rightarrow HF+CO$; run 13/29 of Table A-I.

Figure A.2.3.

HF rotational distributions for $v'=1-4$ from run 13/29 of Table A-I.

$V = 4$

$V = 3$

$V = 2$

$V = 1$

0.0 2.0 4.0 6.0 8.0 10.0 12.0 14.0
ENERGY (KCAL/MOL)

for reaction [8] have been obtained.

(b) $F + HCO$ -- experimental results

When the reagent flows are increased and/or the injector is withdrawn, emission is seen from HF vibrational states energetically inaccessible to reaction [8]. In the highest flow, highest injector location experiments reported here, emission was recorded from all HF vibrational levels ≤ 10 . The levels $5 \leq v \leq 10$ can only be populated by the secondary reaction, [6]; levels $v \leq 4$ are accessible to both [8] and [6]. Consequently, in the following analysis, the levels $v \geq 5$ will be considered separately from those ≤ 4 .

For those experiments in which HF emission from ≥ 5 was seen, infrared emission was also observed from vibrationally-excited CO ($v' \leq 5$). The emission intensities of the high- v HF and the CO behaved in the same manner as a function of reagent flows and injector location. No CO^+ was observed unless the high v -levels of HF were also seen. The origins of the two types of emission are thus believed to be the same.

Figure A.2.4 shows a portion of the HF spectrum recorded under conditions in which the secondary reaction occurs, taken at a resolution of 0.48 cm^{-1} . The P-branches of the vibrational levels $v' = 5-9$ have been assigned, giving an indication of the signal-to-noise ratio for each. The CO region of a spectrum taken under the same experimental conditions is shown in figure A.2.5. This spectrum was taken at a higher resolution: 0.06 cm^{-1} . The individual rovibrational lines are clearly resolved at this resolution, in spite

Figure A.2.4.

A portion of the HF emission spectrum recorded under conditions of high F-atom concentration. The P-branch transitions of v-levels 5-9 are indicated. These levels are energetically inaccessible to the primary reaction.

Figure A.2.5.

The CO emission observed under the conditions of the previous figure. The spectral resolution is 0.06 cm^{-1} . HF emission lines from high (V,J) states are also seen at the high frequency end of the spectrum.

of the low rotational constant for CO (1.9557 cm^{-1} ; (29)). For the sake of clarity, only the band origins and P- and R-branch ranges are indicated. No emission was seen from CO vibrational levels greater than $v' = 5'$ the intensity drops monotonically with v -level until it sinks into the noise.

The HF vibrational distributions derived from spectra such as that shown in figure A.2.4 are given in Tables A-II (reagent inlet configuration A) and A-III (reagent inlet configuration B). The experimental conditions (reagent flows, injector position) and total populations are also given for each run.

Comparing the results from the two different reagent inlet configurations, it can be seen that, using configuration B, emission from the secondary reaction, [6], could not be eliminated, even at the lowest flows and injector location used (experiment 5/38). For all experiments in Table A-III, however, the injector was inside tube 1. As F-atoms were flowing in this tube as well as in tube 2, the F-atom density at the reagent mixing region was greater than for the case where the injection point was three cm. below both outer tubes (reagent inlet configuration A; experiment 13/29).

In spite of this difference, the tables show that the vibrational distributions for the lower ($v \leq 4$) v -levels obtained in these experiments are fairly insensitive to the inlet configuration used (A or B) and to reagent flows (within certain limits), but quite sensitive to the injector location. Thus, increasing the flow of

Table A-II

Results for all HF v-levels; reagent inlet configuration A

RUN #	SF ₆ ^{a,b}	H ₂ CO ^a	I.P. ^c	P(v'=1)	2	3	4	5	6	7	8	9	10 ^d)	P _{tot}
13/29	1.3	0.67	-3.0	0.22	0.24	0.33	0.20							0.095
13/30	1.8	0.67	-0.5	0.16	0.30	0.35	0.19							0.136
13/31	11.8	0.67	-0.5	0.15	0.26	0.34	0.21	0.019	0.014	0.011				1.46
13/32	11.8	2.1	-0.5	0.14	0.25	0.34	0.20	0.027	0.018	0.014	0.009	0.003		3.99
13/33	23.6	2.2	-0.5	0.12	0.25	0.34	0.20	0.029	0.021	0.015	0.009	0.005		15.1
13/34	23.6	3.9	-0.5	0.12	0.25	0.34	0.20	0.033	0.022	0.017	0.010	0.005	0.001	25.7
13/35	21.8	4.3	+0.5	0.17	0.29	0.29	0.15	0.044	0.024	0.015	0.008	0.004	0.001	33.4
13/36	21.0	10	+0.5	0.16	0.29	0.29	0.16	0.042	0.025	0.017	0.010	0.003	0.001	109

a) Flows in micromoles/sec.

b) Discharge in Tubes 1 and 2

c) Injector distances inside Tubes 1 and 2 (cm). Negative values indicate that the injector was below the outer tubes.

d) The v'=10 relative populations are lower limits only. See text.

Table A-III

Results for all HF v-levels; reagent inlet configuration B

RUN #	SF ₆ ^{a,b}	H ₂ CO ^a	I.P. ^c	P(v'=1)	2	3	4	5	6	7	.8	9	P _{tot}
5/38	3.7	1.1	-2.1	.15	.31	.34	.17	.012	.008				.219
5/39	3.8	1.1	-0.1	.15	.30	.32	.16	.033	.022	.012			.399
5/40	3.8	1.1	+0.4	.16	.30	.31	.15	.037	.024	.014			.408
5/41	14	1.1	+0.4	.18	.33	.28	.12	.040	.027	.015	.008		1.177
5/42	14	1.1	-2.1	.13	.28	.33	.17	.033	.028	.018	.010		.705
5/43	14	5.0	-2.1	.12	.27	.33	.18	.034	.025	.019	.012	.007	2.667
5/44	14	5.0	0.4	.16	.30	.30	.14	.043	.028	.018	.011	.007	3.720
5/45	14	2.6	0.4	.15	.30	.30	.14	.044	.029	.019	.012	.007	2.172
5/46	14	2.6	-2.1	.11	.27	.33	.18	.035	.026	.016	.011	.008	1.545

a) Flows in micromoles/sec.

b) Discharge in both Tubes 1 and 2.

c) Distance inside Tube 2 (cm). Negative values indicate that the injector was below this tube.

SF_6 , with the injector outside tube 2 (reagent inlet configuration B) caused an increase in the total emission intensity (in a non-linear fashion) and emission from HF v-levels ≥ 5 , but no change in the distribution of the lower v-levels. This is illustrated in figure A.2.6, which shows the total populations vs. v-level for runs 5/38 and 5/42 of table A-III. The same effect can be seen by comparing runs 13/30 and 13/31, or 13/32 and 13/33, all from table A-II. An increase in the flow of H_2CO also leads to an increase in total population, but no real change in the vibrational distribution. This is illustrated by reference to runs 5/42, 5/46 and 5/43 (or 5/41, 45, 44), of table A-III, and to figure A.2.7 in which the flow of H_2CO is increased from 1.1 $\mu\text{mol/sec}$ to 5.0 $\mu\text{mol/sec}$, with no change in the distributions. Another, more striking demonstration of this is given by comparing runs 13/35 and 13/36 (table A-II), where the flow is increased from 4.3 to > 10 $\mu\text{mol/sec}$, again with no change in the vibrational distributions.

The position of the injector has a strong influence on the distributions, though. For both inlet configurations, it can be seen that withdrawing the injector inside tube 2 causes a noticeable vibrational deactivation of the HF. This is illustrated by reference to runs 5/43 and 5/44 or 5/45 and 5/46 in Table A-III and runs 13/34 and 13/35, in Table A-II. That this is mainly due to the increased number of wall collisions suffered by the HF, rather than a gas phase effect, is demonstrated by runs 5/44 and 5/45 or 5/43 and 5/46 of table A-III. An increase in flows (and thus pressure in the mixing zone) causes no extra deactivation, i.e.,

Figure A.2.6.

HF vibrational populations from Table A-III, showing the effect on these of increasing the SF_6 flow from $3.7 \mu\text{mol/s}$ (5/38) to $14 \mu\text{mol/s}$ (5/42) with all other conditions constant. An increase in total population and emission from high ($v' > 5$) v -levels is observed.

Figure A.2.7.

HF vibrational populations from Table A-III, showing the effect of increasing the H_2CO flow from 1.1 (5/42) to 2.6 (5/46) to 5.0. (5/43) $\mu\text{mol/s}$, all other conditions being constant. An increase in total population, with no change in the distribution is the result.

the flow dependence of the distributions is the same for the injector inside or outside tube 2. The effect of the injector location (inside or outside tube 2) is illustrated for runs 5/43 and 5/44 in figure A.2.8. As expected, the total population increases as the injector is withdrawn. As mentioned earlier, this is due to the greater density of atomic reagent near the bottom of tube 2. The deactivating effect is clearly shown however.

Tables A-IV and A-V give the HF vibrational distributions in the high v -levels for the two inlet configurations, renormalized such that $\sum_{v'=5}^9 P_{v'} = 1.0$. The same dependence on reagent flows and injector location is observed for the high- v distributions as was seen for the complete ones. Figures A.2.9, A.2.10 and A.2.11 show, respectively, the effect of increasing SF_6 flow, increasing H_2CO flow and withdrawing the injection point inside tube 2 for the higher levels. The data plotted in these figures is the same as that shown in the corresponding plots of the complete distributions, discussed above.

Figure A.2.12 shows the rotational distributions in the low ($v' \leq 4$) vibrational levels for run 5/43 (table A-III). A strong 300 K Boltzmann contribution to the distribution is apparent for each level, as well as a long "tail" of populated J -levels, extending to much higher J -values than are populated by the primary reaction. This is in marked contrast to the distributions shown in figure A.2.3 in which rotational relaxation appears to have been almost arrested. The rotational distributions for v -levels 5-9, displayed in figure A.2.13 however, do not have a strong Boltzmann contribution. They are all very broad distributions, resembling the higher- J portions of the lower v -levels in this respect. The same was true for all

Figure A.2.8.

HF vibrational populations from Table A-III, showing the effect of raising the injection point, while keeping all flows constant. Run 5/44 (injector inside Tube 2) is clearly more relaxed than run 5/43 (injector outside Tube 2).

Table A-IVResults for HF($v'=5-10$); reagent inlet configuration A

RUN #	SF ₆ ^{a,b}	H ₂ CO ^a	I.P. ^c	P($v'=5$)	6	7	8	9	10	P _{tot}
13/31	11.8	0.67	-0.5	0.51	0.27	0.22	0.			0.02
13/32	11.8	2.1	-0.5	0.38	0.25	0.19	0.13	0.05		0.11
13/33	23.6	2.2	-0.5	0.37	0.25	0.19	0.11	0.06		0.80
13/34	23.6	3.9	-0.5	0.37	0.25	0.19	0.11	0.06	0.01	1.4
13/35	21.8	4.3	+0.5	0.46	0.25	0.16	0.08	0.04	0.008	1.7
13/36	21.0	10	+0.5	0.43	0.26	0.17	0.10	0.03	0.005	6.2

a) Flows in micromoles/sec

b) Discharge in Tubes 1 and 2

c) Injector distance inside Tubes 1 and 2, in cm. Negative values indicate that the injector was below the outer tubes.

Table A-V

Results for HF(v'=5-9); reagent inlet configuration B

RUN #	SF ₆ ^{a,b}	H ₂ CO ^a	I.P. ^c	P(v'=5	6	7	8	9	p _{tot}
5/38	3.7	1.1	-2.1	.57	.43				.00450
5/39	3.8	1.1	-0.1	.49	.33	.18			.0268
5/40	3.8	1.1	0.4	.49	.32	.19			.0307
5/41	14	1.1	0.4	.44	.29	.17	.10		.107
5/42	14	1.1	-2.1	.36	.32	.20	.11		.063
5/43	14	5.0	-2.1	.35	.26	.20	.12	.077	.259
5/44	14	5.0	0.4	.40	.26	.16	.10	.069	.398
5/45	14	2.6	0.4	.39	.26	.17	.11	.065	.242
5/46	14	2.6	-2.1	.36	.28	.17	.11	.083	.149

a) Flows in micromoles/sec.

b) Discharge in both Tubes 1 and 2.

c) Injectors distance inside Tube 2.

Figure A.2.9:

The high v -level ($v' > 5$) portion of Figure A.2.6, from Table A-V, showing the effect on these levels of increasing the SF_6 flow.

Figure A.2.10.

The high v-level portion of Figure A.2.7, from Table A-V, showing the effect on these levels of increasing the H_2CO flow. An increase in total population with no change (outside experimental error) in the distribution is the result.

Figure A.2.11.

The high-v portion of Figure A.2.8, from Table A-V, showing the effect on these levels of raising the injection point from outside (5/43) to inside (5/44) Tube 2. A noticeable deactivation is the result.

Figure A.2.12

HF rotational distributions for $v'=1-4$ from run 5/43 of Table A-III, to compare with Figure A.2.3. The high-J "tails" and a Boltzman component to the distributions are apparent.

$V = 4$

$V = 3$

$V = 2$

$V = 1$

Figure A.2.13

HF rotational distributions for $v'=5-9$ from run 5/43 of Table A-III.

$V=9$

$V=8$

$V=7$

$V=6$

$V=5$

0.0 5.0 10.0 15.0 20.0
ENERGY (KCAL/MOL)

of the high- v rotational distributions observed in these experiments.

The CO vibrational distributions were found to be considerably less sensitive to the experimental conditions than those of HF.

Table A-VI presents the results of some representative experiments.

Comparing runs 5/43 and 5/45, it can be seen that whereas the HF becomes somewhat vibrationally relaxed upon raising the injector (Table A-III), the CO distribution remains essentially constant. The same can be said of the dependence of the distribution on reagent flows; the total population increases with increased reagent flow (and upon raising the injector), but the distribution remains constant. This observation indicates that a substantial proportion of the atom/radical reaction must take place in the low-pressure region of the apparatus, below the reagent inlet.

The spectra from which these results were derived were taken at a resolution of 0.48 cm^{-1} . At this resolution, because of the small rotational constant for CO, many emission lines were overlapped.

In order to resolve the spectrum more fully and thus obtain a more accurate vibrational distribution, a single spectrum was taken at 0.06 cm^{-1} resolution (shown in figure A.2.5). To increase the signal-to-noise ratio, this experiment was done using reagent inlet configuration B and the injector even with the bottom of tube 2.

As demonstrated in the previous table, this injector position was expected to yield results different only in emission intensity from an experiment having the injector lower. Immediately previous to this high-resolution experiment, a spectrum was taken at 0.48 cm^{-1}

Table A-VI
CO vibrational distributions

RUN #	SF ₆ ^{a,b}	H ₂ CO ^a	Inlet Configuration	I.P. ^c	v'=1	v'=2	v'=3	v'=4	v'=5
5/36	3.4	7.5	A	0.75	.53	.26	.10	.05	.06
5/43	14	5.0	B	-2.1	.53	.24	.12	.08	.02
5/45	14	2.6	B	+0.4	.53	.25	.13	.07	.02

a) Flows in micromoles/sec

b) Discharge in both Tubes 1 and 2

c) Injection position in cm. Negative values indicate that injector was below Tube 2.

resolution, under the same conditions. From this, the HF distributions were calculated. Table A-VII gives the full experimental conditions and vibrational distributions of both excited species.

The higher-resolution spectrum gives the same distributions in both products as do those taken at lower resolution under the same experimental conditions (c.f. table A-III). Figure A.2.14 shows the CO vibrational distributions vs. v-level for all the CO experiments discussed here. The spread of values in each level gives an indication of the error associated with the measured distributions.

The CO rotational distributions derived from run 11/5 are shown in figure A.2.15. They, like those of the high-v HF, are quite broad and do not show a sizeable Boltzmann peak at low J-values. Again, as for HF, the rotational distributions did not change substantially with experimental conditions. This information should be treated cautiously, however, as the resolution used for the majority of the experiments did not completely resolve all rotational lines in the spectra.

(c) Discussion of results

The total energy available to products in reaction [6] may be calculated (56) from:

$$E'_{\text{tot}} = -\Delta H_0^0 + E_a + 3RT$$

where ΔH_0^0 is the heat of reaction at 0K, E_a is the activation energy and $3RT$ is the (average) thermal energy (both translational and

Table A-VII

Results of high resolution CO experiments

$\text{SF}_6^{a,b}$	H_2CO^a	IP-1 ^c	IP-0 ^d	$P(v'=5)$	6	HF 7	8	9)	$P(v'=1)$	2	CO 3	4	5)
2.9	2.1	0.0	+2.0	.42	.28	.16	.10	.05	.53	.22	.12	.09	.04

a) Flows in micromoles/sec

b) Discharge in both Tubes 1 and 2

c) Injector distance inside Tube 2

d) Injector distance inside Tube 1

Figure A.2.14

CO vibrational distributions, given in Tables A-VI and A-VII. The insensitivity of the distribution to the experimental conditions is clear.

Figure A.2.15

CO rotational distributions for $v'=1-5$, from run 11/5 of Table A-VII.

$V = 5$

$V = 4$

$V = 3$

$V = 2$

$V = 1$

rotational) brought to the reaction by the reagents. This assumes that there is no vibrational excitation of the molecular reagent; in this case, the HCO formed in reaction [8]. It has been suggested (53) that this reaction produces vibrationally excited HCO, with one quantum deposited in the ν_1 (H-CO stretch) mode. The evidence for this was contained in the HF rotational distributions observed by Macdonald and Sloan. These were quite broad and displayed two maxima: that corresponding to a Boltzmann distribution of HF rotators at the temperature of the molecular reagent and a second, less intense one at higher J-values. As such, they are qualitatively different from the ones observed in this work, when no HF($v' \geq 5$) was seen. However, in view of the poor signal-to-noise in the latter experiments (i.e., those given in Table A-1), no conclusion can be drawn from these results as to the formation of HCO⁺ in the present experiments.

If the formyl radical is formed in a vibrationally-excited state, it is likely that it reacts prior to being deactivated. The rate constant for deactivation of one quantum of bending vibration in HCO by formaldehyde has been measured (47) to be $(4.3 \pm 1) \times 10^{-12}$ cc/molec/sec. Assuming that the ν_1 mode is deactivated by collisions with formaldehyde with a rate constant two orders of magnitude larger than for the bend, brings the rate constant for deactivation about equal to that expected for reaction. However, under conditions such that the products of the radical reaction are observed, the F-atoms are in excess over formaldehyde in the reaction zone. Thus, even assuming a gas kinetic rate constant for vibrational deactivation, reaction will still be the faster loss process for the excited HCO

radicals. As there is no evidence either for or against the production of vibrationally-excited HCO radicals in the present work, it is assumed in the following that these radicals are formed vibrationally cold. This is also consistent with the high fraction of total energy of the primary reaction which appears as HF vibration (about 50-60% (53,56,57b)).

The heat of formation of HCO, required in order to calculate ΔH_0^0 , is not well known. Okabe (59) gives three values, ranging from -3 ± 3 (60) to $+10.3 \pm 2$ kcal/mol (61). His own estimate is $+3.7 \pm 1.5$ kcal/mol (59). From the heat of reaction of the process: $\text{HCO} \rightarrow \text{H} + \text{CO}$ $\Delta H_{300}^0 = 15.5 \pm 1.5$ kcal/mol (45) and the known heats of formation of H-atoms and CO (60), the $\Delta H_{300,f}^0$ for HCO may be estimated as $+8.9 \pm 1.5$ kcal/mol. If a value of 4 kcal/mol is chosen for the heat of formation and zero activation energy assumed for this atom-radical process (47,48), the total energy available to products becomes 116 kcal/mol. This is enough to populate HF in ro-vibrational states up to ($v' = 13$, $J' = 10$) and CO up to ($v' = 21$, $J' = 25$).

The observed distributions did not extend to the maximum levels calculated in this manner. The highest HF state recorded in this work was ($v' = 10$, $J' = 2$). However, because the vibrational distribution decreases monotonically with v-level this turned out to be the place where the signal sank below the noise. This region of the spectrum also suffers from strong atmospheric CO₂ absorption;

the CO emission lines begin here as well. The possibility is not ruled out, then, that HF levels are populated up to the thermochemical limit by reaction [6].

The CO vibrational distribution is much less broad than that of HF; only the first five levels are populated. As can be seen in figure A.2.5, any v -levels higher than this maximum are lost in the noise. Because the cutoff of the InSb detector used lies at around 1850 cm^{-1} , an experiment was done using the HgCdTe detector, which has a cutoff in the region of 1400 cm^{-1} . Again, no CO emission from $v' > 5$ was observed.

The fact that the HF vibrational populations should decrease with v -level is somewhat surprising, in view of the very large exoergicity of [6]: In most light-atom transfer reactions, $A + H-B \rightarrow AH + B$, in which a light species (generally H) is transferred between two heavier moieties, it has been found that a significant portion of the reaction energy is partitioned into vibration of the newly-formed molecule (4). This has been interpreted, for the three-body case with this mass combination, as being indicative of mixed energy release on a repulsive potential energy surface (PES)⁽⁶²⁾. This means that the H-atom is transferred impulsively while the reagents are still far apart. A large fraction of the reaction energy (which is released as products separate on a repulsive PES), is thus channeled into vibrational motion in the nascent A-H bond.

Monotonically decreasing HF vibrational distributions have been observed for some highly-exoergic systems, however (8-10,13). These have been interpreted as being due to the formation of an

intermediate complex which is long-lived with respect to the vibrational period associated with motion along the reaction coordinate. Under these circumstances, energy which is initially deposited in the newly formed HF bond is randomized to some extent over the entire complex. If the complex lives long enough, the reaction energy may be partitioned statistically among all of its degrees of freedom. This may occur if, for instance, the intermediate complex corresponds to a (highly excited) bound molecule. The resulting product energy distributions are then those expected for the collisionless unimolecular decay of the complex.

In the F/HCO system, such a long lived intermediate is possible. The formyl fluoride (FHCO) molecule is stable and well known (43,59,63,64).

The ground state (X^1A' ; C_s) (here both the term symbol and the symmetry group are given) correlates directly to both reactants: $F(^2P)$, $HCO(X, ^2A'; C_s)$ and to products: $HF(^1\Sigma^+; C_{\infty v})$, $CO(^1\Sigma^+; C_{\infty v})$.

A barrier to the dissociation reaction:

of 58 kcal/mol has been determined theoretically (65,66). A schematic correlation diagram, incorporating these features, is shown in figure A.2.16.

The figure shows that (in C_s symmetry) there is only one spin- and orbitally-allowed PES connecting ground state reactants and products. This is the surface which also correlates to ground state FHCO; it thus contains a deep potential energy well. The system, of course, is not constrained to react in C_s symmetry, but as noted previously,

2

Figure A.2.16

Schematic correlation diagram in C_s symmetry, for the F/HCO system. The $1A'$ surface is the only one connecting ground state reactants and products. The transition state is that of Morokuma (65,66).

the presence of the deep energy well is expected to influence the dynamics strongly.

The possibility arises, then, that the observed product distributions are the result of a statistical partitioning of excitation energy, following the unimolecular dissociation of chemically-activated FHC0. Calculations were thus carried out to predict the distributions expected from this statistical process. The method used to calculate the statistical distributions has been previously described (8b,19).

The method is based upon the phase space theory of Light et al (67). This theory assumes that the frequency with which a given product state, S, will be populated is proportional to the density of all other product states consistent with the formation of S. The relative probability that the state S will be formed is thus:

$$P^0(E'_{\text{tot}}, J; S) = N(E'_{\text{tot}}, J; S) / \sum_S N(E'_{\text{tot}}, J; S).$$

In this expression, $N(E'_{\text{tot}}, J; S)$ is the number of product states energetically accessible after populating S, J is the total angular momentum of the system (orbital and rotational) and E'_{tot} is the total energy available.

For a given product molecule (HF or CO) the density of states calculation is carried out as follows. First, a ro-vibrational state of the product of interest is specified. The energy of this state is calculated very accurately by means of a Dunham expansion containing seventeen coefficients in the case of HF and ten for CO (29). The number of states of the other fragment (CO or HF)

which could be populated was then calculated, using a direct-count procedure for the first few thousand wavenumbers and the Whitten-Rabinovitch approximation thereafter. The latter state energies were not calculated exactly, but were approximated by a harmonic oscillator with one anharmonicity term. The rotational energy densities were calculated by inversion of the classical partition function⁽⁶⁸⁾.

Angular momentum must be conserved (on average) over the course of the reaction; this condition was fulfilled as follows. The total angular momentum of the reagents was calculated as the vector sum of rotational, $J(\text{HCO})$, and orbital, $L = \mu \bar{v} b$, angular momenta. In the expression for L , μ is the reduced mass for the collision, $\bar{v}$ is the average velocity and b , the maximum impact parameter. The average thermal rotational energy of the HCO was given by: $CJ(J + 1) = kT/2$, where C for HCO was taken as being equal to the CO rotational constant. The maximum impact parameter, b , was an input parameter to the calculation, but was held constant at $5\text{\AA}$. (This choice will be discussed below).

The total angular momentum of the products, was the vector sum of the rotational angular momenta of the HF and CO products and the product orbital angular momentum: $L' = \mu' \bar{v}' b'$. In practice, the amount of orbital angular momentum created by the reaction, i.e. the ratio L'/L , was treated as a variable parameter.

The nature of this calculation makes it very sensitive to the vibrational frequency of the product of interest. This frequency corresponds to the one which that product has in the region of the

PES at which the energy is distributed. It is thus the density of states at this point which determines the probability of populating a given product state. RRKM calculations have shown that the exact choice of transition state frequencies plays a major role in the results.

If, in this case, it is assumed that energy partitioning takes place far enough into the exit channel that the asymptotic HF and CO frequencies (i.e., those of the isolated molecules) are appropriate for the density of states calculation, the results are those shown in figures A.2.17 (for HF) and A.2.18 (for CO). This assumption requires that the HF-CO intermediate be loosely-bound, but still have a free flow of energy between the two fragments. That is, the coupling between the fragments is strong enough to permit the free flow of energy between them, but not so strong as to perturb their vibrational frequencies.

In each figure the experimentally-determined distributions are shown as points; the error bars correspond to the estimated error of $\pm 2\%$ on each v-level. The two solid lines give the results under two extreme assumptions concerning the creation of orbital angular momentum in the reaction. In one, it is assumed that the final impact parameter is always zero. The other assumes no limit, apart from that imposed by the total energy (and hence angular energy), to the final orbital angular momentum. Any real system, of course, lies somewhere in between the two extremes. In these calculations, the initial maximum impact parameter, b , was chosen to be $5\text{\AA}$.

Figure A.2.17.

HF vibrational distribution for $v'=5-9$ of run 5/43 (Table A-V) (shown as squares) and the statistical prediction using the isolated-molecule vibrational frequencies in the density of states calculation (shown as solid lines). The two lines correspond to the two assumptions regarding angular momentum constraints (see text). The predicted distribution is colder than that observed.

Figure A.2.18:

CO vibrational distribution of run 11/5 (Table A-VII), shown as squares and the statistical prediction, using the isolated-molecule vibrational frequencies (solid lines). The predicted distribution is clearly more excited than the measured one.

This value was used to match that found for the system

studied both theoretically⁽⁵⁰⁾ and experimentally⁽⁴⁷⁾. Using values ranging between 3 and 5⁰_A in the calculation, however, gave rise to virtually identical statistical distributions.

The prediction for HF is seen in figure A.2.17 to lie fairly close to the observed distribution. It does, however, consistently underestimate the amount of excitation seen experimentally. Even including the estimated error of $\pm 2\%$ on the experimental measurements (shown as error bars in the figure), the experimental distribution lies outside the range predicted by the phase space calculation, using the isolated HF frequency. This strongly implies that the energy is partitioned before the products take on their asymptotic vibrational frequencies; that is, that there is a stronger coupling between them than was assumed for this calculation.

The prediction for CO, using this model, is shown in figure A.2.18. Because of the larger amount of phase space available to the CO with respect to HF, (due to its smaller vibrational frequency) the calculated distributions are less strongly decreasing than those of HF. The figure shows that the measured distribution is considerably colder than that calculated using this model. This is not due to relaxation of the CO. As was discussed in the previous section, the CO distribution was not affected by injector location or reagent flows; the observed CO vibrational distribution is assumed to be

the correct, nascent one. Thus it is concluded that the energy partitioned into vibration of the nascent CO is, like that of the HF, not that expected on the basis of a statistical distribution over product states having the isolated frequencies.

Another, more realistic, assumption regarding the place at which the energy is partitioned can be made. The energy of the FHC0 complex may be distributed among the product modes in a region of the PES where the HF and CO are more strongly coupled. If this coupling is strong enough, the vibrational frequencies of interest are not those of the isolated molecules but those modes of the complex which correlate to the vibrations of the products, as the latter separate. These are the frequencies that determine the densities of states in the phase space calculation. The problem with this approach, of course, is that the vibrational frequencies of chemical intermediates are not known experimentally and very few high-level theoretical calculations of them exist.

Recently, the HF distribution from the reaction:

has been interpreted by this method⁽⁸⁾. The frequencies at the transition state for the unimolecular decomposition of vinyl fluoride had been published by Morokuma⁽⁹⁾. Using these frequencies and the method described above, excellent fits to the experimental data were obtained. Such agreement was not obtained using the isolated-product vibrational frequencies. For the vinyl fluoride

system, the calculated transition state frequency for HF was 1000-2000 cm^{-1} lower than that of the isolated molecule (8b,69). This implies that a larger volume of phase space is available to the HF when the energy is being partitioned. As a result of this larger volume of phase space, the calculated statistical vibrational distribution decreases relatively slowly with v-level. The distribution calculated in this manner matches that of the experiment very closely.

In some recent reports, Morokuma and co-workers^(65,66) have published the intrinsic reaction coordinate (IRC) for the decomposition of formyl fluoride. They also in figure 7 of ref. 65 illustrate the changing frequencies of the FHC₂O normal modes, along this IRC. This figure shows that the CO vibrational frequency changes very little, from reagent to products. The normal mode correlating to HF vibration in products however, changes radically over the IRC. Specifically, at the calculated transition state and well into the exit channel, this frequency is considerably smaller than that of isolated HF. It is approximately 3000 cm^{-1} at the transition state, decreases to a minimum of about 2500 cm^{-1} early in the exit channel, then increases to 4100 cm^{-1} at the isolated product limit.

Another phase space calculation was carried out for the products using the frequencies calculated by Morokuma et al.⁽⁶⁵⁾ for the transition state. The value used for the HF frequency was 3000 cm^{-1} ; the CO frequency, since it changed so little over the IRC, was taken as that of isolated CO. (The calculation of the CO distribution used the lower HF frequency though.) The results of these calculations

are given in figures A.2.19 and A.2.20.

The predicted HF distribution using the transition state frequency is seen to be considerably more excited than that shown in figure A.2.17. The predicted distribution is now somewhat more excited than the measured one. The quality of fit to the experimental data is a little, but not substantially, better than that using the isolated HF frequency. This result shows that whereas the density of states was not high enough, using the frequency of isolated HF, to describe accurately the amount of excitation observed in that product, the density of states at the transition state configuration is too high to do so.

Comparing the two figures for HF (A.2.17 and A.2.19) shows that energy partitioning into HF vibration occurs at a place along the IRC which is between the transition state and the isolated products. Therefore further statistical calculations were carried out, in which the HF frequency (and thus the volume of phase space accessible to the HF) was varied. Using a frequency of 3500 cm^{-1} , a very good match to the measured data was obtained. This is shown in figure A.2.21. Reference to figures 7 and 4 of (65), relates this HF frequency to a position along the reaction coordinate. These figures show that the nascent HF vibrational frequency is 3500 cm^{-1} when the distance between the centres of mass of the two products is $2.3\text{ \AA}$; at this point the HF bond length is $1.12\text{ \AA}$. It should be stressed here that this derived geometry corresponds to an average geometry at which energy partitioning may be said to occur. The important point is that the energy is partitioned during product

Figure A.2.19.

Measured (run 5/43) and statistical HF vibrational distributions using the vibrational frequencies of the Morokuma (65,66) transition state in the density of states calculation. The predicted distribution is now more excited than that observed.

Figure A.2.20.

Measured (11/5) and statistical CO vibrational distributions using the Morokuma (65,66) frequencies. Again, the measured distribution is far less excited than the statistical prediction.

Figure A.2.21.

Measured (run 5/43) and statistical HF vibrational distributions. A vibrational frequency of 3500 cm^{-1} for HF was used in the density of states calculation. The fit to the measured data is excellent.

separation (i.e., after the transition state) and certainly prior to the HF taking up its isolated-molecule frequency.

Figure A.2.20 shows the results for CO, based on the Morokuma (65) transition state HF frequency. There is, in fact, no difference between this prediction and the one based on the isolated HF-molecule frequency. The conclusion, then, is that the measured CO vibrational distribution is not well reproduced by any calculation which assumes statistical distribution of energy among all modes of the reaction products.

This would seem to be inconsistent with the fact that the observed HF distribution can be well matched by a statistical calculation. However, the nature of this phase space calculation makes it considerably less sensitive to the vibrational frequencies of the second product than those of the product of interest. This is because, after specifying a state of the product of interest, the phase space left accessible to the other product is dominated by translations and rotations. These have much smaller energy spacings (and consequently, larger volumes of phase space) associated with them than do the vibrations, unless the vibrational frequency(ies) of that product are diminishingly small. The calculation is thus not overly sensitive to the vibrational frequencies of any product but the one of interest.

A demonstration of this is shown in figure A.2.22. In the figure, the measured HF vibrational distribution is again plotted for comparison to the results of another phase space calculation in which all product modes except the CO vibration were populated

Figure A.2.22.

Measured (run 5/43) and statistical HF vibrational distributions. The isolated-molecule value was used for the HF frequency; no vibration of the CO fragment was allowed in the density of states calculation. The fit to the measured data is again very good.

statistically. Using the vibrational frequency of isolated HF and a value of infinity for the CO vibrational spacing, it is seen that the match with the observed distribution is again excellent.

Thus a model in which there is free flow of energy among HF (but not CO) vibration, rotational motion and relative translation of the centres of mass of both fragments (HF and CO), can also give good agreement with the experimentally-measured HF distribution. This is, of course, a limiting example; the fact that vibrationally-excited CO was observed indicates that the CO vibration participates to some degree in the energy flow between products. However, the calculation does serve to demonstrate clearly that an excellent match to the measured HF distribution can be provided by a phase space calculation in which the nascent CO vibrational levels are not populated statistically.

The rotational distributions of the high- v HF and the CO are quite similar (figures A.2.13 and A.2.15). The low J -levels of HF($v=5,6$) show some evidence of a 300K Boltzmann peak, as do those of CO($v=1,2$). For the most part however, the distributions are broad and flat; rotational relaxation, as indicated by the presence of a 300K Boltzmann peak, seems to have been almost arrested. Figure A.2.23 shows the HF rotational distributions for $v' = 5-9$ of run 13/33 and, superimposed upon them, the predicted statistical distribution, using the value of 3500 cm^{-1} for the HF frequency. If a small amount of rotational relaxation is responsible for the excess population in the lower J -states, the predicted and observed distributions are virtually identical.

Figure A.2.23.

HF rotational distributions for $v'=5-9$ from run 13/33 (Table A-IV) with the statistical prediction (using 3500 cm^{-1} for the HF frequency) superimposed. If some rotational relaxation is assumed, the match to the measured data is quite good.

$V = 9$

$V = 8$

$V = 7$

$V = 6$

$V = 5$

This rotational distribution can be compared to that predicted on the basis of the published IRC for FHC0 decomposition (65,66). As the FHC0 system traverses this IRC, from the reactant state towards the transition state, the FCH angle decreases, shortening the F....H distance. The C-F bond stretches hardly at all between FHC0 and the transition state. Continued motion along the reaction coordinate, from the transition state towards products, results in a further decrease in the F....H distance, with a continued decrease in the FCH angle. This angle eventually passes through 0° (i.e., collinear CFH); at the same time, the C-F distance increases. In this manner, the decomposition is predicted to proceed via a "spinning-off" of the nascent HF from the remaining CO fragment.

According to this model, the HF product of the decomposition of FHC0 is predicted to be rotationally excited. However, the measured rotational distributions show no evidence of specific rotational excitation. Rather, they indicate a statistical population of rotational levels. It must therefore be concluded that while the Morokuma calculation probably gives the correct transition state geometry and subsequent configurations along the IRC, the statistical population of HF vibrational and rotational levels indicates that the free flow of energy among certain modes of the nascent products continues as the complex is decomposing. This has the effect of removing any specificity of product excitation implicit in the calculated (65,66) IRC.

The present results imply very strongly that a greater-than-statistical amount of the reaction energy is partitioned into

relative translation of the products, at the expense of the CO vibration. Similar results were obtained in a trajectory study⁽⁵⁰⁾ of:

on an analytical potential energy surface⁽⁷⁰⁾. For reaction at 300K, it was found that 90% of the reaction energy was given off to the H₂ fragment; 30% appeared as H₂ vibration and 48% as translation. The CO fragment was formed predominantly in its ground vibrational state.

The reason for the less-than-statistical partitioning of reaction energy into the CO fragment observed in the present work lies in the relatively small changes undergone by the geometry of that fragment over the course of the reaction. At the calculated transition state^(65,66), the CO bond length is 1.12 Å. The value for isolated CO is 1.13 Å⁽²⁹⁾. As mentioned previously, the CO frequency is not predicted to change much along the IRC. The HF, on the other hand, undergoes quite radical changes in geometry (the H-F distance at the transition state is given as 1.41 Å^(65,66); that of isolated HF is 0.917 Å⁽²⁹⁾) and frequency as the system traverses the IRC. On this basis, more energy might be expected to be partitioned into the HF vibration than that of CO.

Lin *et al.*^(51,55) investigated the reaction complementary to the one in the present study, *vis*

By flash-photolysing a mixture of SO_2 , CHFBr_2 and an inert buffer gas, they were able to observe laser action from the first three excited vibrational levels of HF. Using a CO laser to probe for that product, they found $\text{CO}(v' \leq 24)$. Both molecular products displayed monotonically-decreasing vibrational distributions. The average energy in vibration was about the same (ca. 15 kcal/mol) for each.

The HF vibrational distribution observed by these authors was well fitted by a statistical calculation, quite similar to the first one discussed herein, but neglecting product rotations (and hence all angular momentum constraints). The CO distribution fell midway between those predicted by that statistical calculation for reactions [11a] and [11b]. This fact, and the results of some scavenger experiments, led the authors to conclude that both reactions were occurring in their system.

Based on these results, they proposed that reaction [11] also occurs via the decomposition of a long-lived FHCO complex. Two major differences exist between that system and the F/HCO one however.

First, the former reaction [11a] has an exoergicity of about 185 kcal/mol - some 70 kcal/mol more than reaction [6]. Second, a CO bond is formed in reactions [11], whereas it already exists in the F/HCO system. These two differences make it hardly surprising that the product energy distributions observed in (51,55) are different from those reported herein.

Based upon the foregoing discussion, it is proposed that reaction [6]:

proceeds via a long-lived FHC0 complex which decomposes along a reaction coordinate similar to the one suggested by Morokuma et al. (65,66) . A statistical partitioning of the reaction energy is observed for the vibrational and rotational degrees of freedom of the HF product. The observed HF vibrational distribution indicates that energy flow between the nascent products remains fast beyond the (calculated) transition state. This conclusion is substantiated by the HF rotational distribution, which does not display the high degree of rotational excitation implied by a decomposition of FHC0 strictly along the IRC calculated in (65,66) . The CO vibrational distribution is not as excited as that expected of a statistical decomposition, however. The conclusion is thus that there is a greater -than-statistical amount of the reaction energy partitioned into relative translation of the two products, at the expense of vibration in the CO. This is probably due to the relatively small changes in the properties of the CO moiety as the system traverses the reaction coordinate.

Chapter A.3: The Reaction $F + NH_2 \rightarrow HF + NH$

A.3.1

INTRODUCTION

A large part of the following chapter is taken from a paper entitled "Vibrational Energy Partitioning in the Reaction of F Atoms with NH_3 and ND_3 "⁽¹²⁾.

In the previous chapter, a system was discussed in which the occurrence of a secondary reaction was demonstrated by the appearance of product energy levels inaccessible to the primary reaction. This simplified the study of the dynamics in two ways. First, it provided unambiguous evidence that the secondary radical reaction did, in fact, occur. Second, due to the large difference in the exoergicities of the radical-generating and radical reactions, several product vibrational levels were populated by the latter, without interference from the former. This allowed the extraction of the contribution to the product energy distributions from the secondary reaction.

Such ease of interpretation is not always the case, however. In this chapter, the results of extensive work on the $\text{F} + \text{NH}_3/\text{NH}_2$ system will be discussed. It will be demonstrated that the radical reaction is considerably faster than the primary reaction (which is already very fast⁽⁷¹⁾). Also, it will be shown that the HF energy distributions from the primary reaction are, unless great care is taken in their measurement, "contaminated" by contributions from the radical reaction. The results indicate that, at least for the production of NH_2 by the reaction of ammonia with F-atoms (vide infra), the energy disposal in the reaction:

[1]

is very specific.

The reaction of F-atoms with ammonia:

which was used to generate the NH_2 radicals, has an exoergicity at 0K of 29 kcal/mol⁽⁵⁹⁾. This by itself is not sufficient energy to populate $v' = 3$ of HF; if reagent translational and internal energy and an activation energy < 1 kcal/mol are included, this level becomes just accessible. The subsequent reaction between F-atoms and amino radicals producing ground electronic state products, has an exoergicity of 44 kcal/mol⁽⁵⁹⁾ - sufficient to populate HF ($v' = 4$). There is thus a maximum of 2 v-levels in HF which may be populated by the secondary, but ~~not~~ the primary, reaction. If conditions are such that both reactions are occurring, the observed product energy distributions will be the sum of those arising from the two reactions. With only one or two HF v-levels unambiguously assignable to the secondary reaction, it becomes very difficult to extract the product energy distributions for each of the reactions from the observed data.

Reaction [2] and its isotopic analogue:

have been the object of some discussion in the recent literature^(3,17,18,72). Specifically, the HF vibrational energy distributions obtained from [2] seem to depend upon the manner in which the experiment is performed. In low pressure, arrested-relaxation machines^(72,17,18), a vibrationally cold (non-inverted) distribution is seen, with a population ratio

$v' = 1/v' = 2$ of about 0.6/0.4. The reaction with ND_3 was initially reported to give a strongly-inverted vibrational distribution in the product $\text{DF}^{(17)}$, with $P(v' = 1:2:3) = 0.20:0.33:0.47$. In fast-flow, measured-relaxation experiments, however, no isotopic difference is observed⁽³⁾. When measured using that technique, both reaction [2] and [2a] are reported to yield strongly inverted $\text{HF}(\text{DF})$ vibrational distributions. The reported distributions are⁽³⁾, for HF : $P(v' = 1:2:3) = 0.33:0.56:0.12$ and for DF , $P(v' = 1:2:3) = 0.15:0.40:0.45$. This result also shows population in $v' = 3$, which, as indicated earlier, is only just accessible to thermal reagents.

These conflicting results, both entirely reproducible in the types of apparatus which generated them, give some indication of the difficulties which can arise in measuring energy disposal in atom/polyatomic systems. In general, these measurements suffer from two complications which are not present (or present to much smaller degree) in atom/diatomic systems. These are, first, the more efficient deactivation of product internal states by the polyatomic molecule, due to the increased number of degrees of freedom which can accept energy. The second complication is the possibility of secondary reaction between the (radical) product of the primary reaction and the excess reagent.

In the following, it will be demonstrated that these complicating processes plague the F/NH_3 system. It will also be shown that the effects can be separately identified and measured. In particular, it will be argued that:

- 1) The F/NH_3 reaction gives rise to a non-inverted vibrational distribution in the HF product.
- 2) There are no inexplicable relaxation effects associated with low reagent flows ⁽³⁾ operating in this system and
- 3) The secondary reaction:

gives rise to a strongly inverted HF vibrational distribution, peaking in $v' = 2$.

In the process of making these measurements, it was found that another complicating factor in the system is a very efficient de-activation of vibrationally excited HF, by ammonia or ammonium fluoride on the walls of the reagent inlet, if ammonia is admitted to the apparatus. This effect manifested itself as a gradual change in the observed energy distribution of the F/NH_3 system, for identical experimental conditions, as a function of time. Specifically, it was found that when ammonia had been flowing in the system, the observed vibrational distributions became progressively and irreversibly more excited with time. The lack of reproducibility of the data which this effect produced was the most puzzling and frustrating aspect of this work; when the cause of the temporal change in the measured distributions was discovered and appropriate corrective steps taken, the interpretation of the results became quite straightforward.

A.3.2

EXPERIMENTAL

Two different reagent inlet configurations were used for these experiments. The first was identical to configuration A of the last chapter; two different injector lengths were used such that the lowest injector position was either 3 or 2 cm below the bottoms of the tubes 1 and 2 (which were even with one another). The second was similar to configuration B. In this case, tube 2 ended 2.3 cm inside tube 1 and the injector, at its lowest position, was 0.2 cm inside tube 1. It was not necessary, in these experiments, to introduce F-atoms via both tubes 1 and 2. For the most part, therefore, the F atoms were flowing in tube 2 only; for one very low atom-density experiment they were allowed to flow in tube 1 only.

Tube 1 was primarily used in these experiments to introduce molecular reagents and relaxation partners to the apparatus. Because energy transfer plays such a large role in the F/NH_3 system and because of the above-mentioned relaxation effects due to wall coatings, experiments were undertaken to investigate the effects of gas phase and wall collisions of vibrationally excited HF in the present apparatus. These were carried out as follows:

The line leading to the injector was equipped with a four-way stopcock, permitting rapid switching between two reagent flows; one directed to the injector and the other to a small mechanical vacuum pump. For the energy transfer measurements, the two reagents were H_2 and D_2 . The flows of both were held constant by electronic flow controllers (Matheson Co. Model 8249) in the inverse ratio of their

rate constants for reaction with F-atoms. This ensured that there was no change in the consumption of these atoms upon switching from H_2 to D_2 . SF_6 was introduced through tube 2; its flow was held constant manually. Experiments were carried out in pairs of runs - one with and one without NH_3 flowing in tube 1. In each of these runs, H_2 and D_2 were switched alternately into the injector and the resulting HF or DF emission measured. The measurement consisted of collecting 25 interferograms with H_2 flowing, switching to D_2 , collecting 25 interferograms, switching to H_2 , etc., until a total of 200 interferograms had been collected. The four sets of 25 interferograms corresponding to each reagent were then co-added; the end result was two spectra - one of the $F/H_2/NH_3$ system and one of $F/D_2/NH_3$. This procedure was repeated several times, varying the flow of ammonia between each. Both immediately prior to and immediately following each run with ammonia flowing, the switching experiment was carried out with no ammonia present.

In this way a total of four spectra (and hence vibrational distributions) were obtained from each cycle of the switching experiment. These corresponded to the reaction systems: (a) F/H_2 , (b) F/D_2 , (c) $F/H_2/NH_3$ and (d) $F/D_2/NH_3$. (a) and (b) served as controls to show what changes had occurred in the apparatus during the previous cycle. Subtracting the HF populations in (d) from those in (c) removed the contribution of the $F + NH_3$ reaction to the HF distributions measured in (c). The difference thus gives the HF vibrational distribution from the $F + H_2$ reaction. Since this distribution is measured in the presence of ammonia, the observed

HF product has suffered the gas phase energy transfer resulting from collisions with ammonia. Comparing this result with the distribution from (a) showed the extent of gas phase vibrational deactivation of HF by NH_3 .

An identical experiment was carried out, using CO_2 in the place of NH_3 . This was done so as to have a reference system, for which the energy transfer with HF is well understood⁽⁷⁷⁾ to which the ammonia information could be compared. This also gave information about the performance of the apparatus in this kind of experiment.

The F-atom precursor in all these experiments was SF_6 (Matheson 99.99% stated purity). Both NH_3 (Matheson 99.99% minimum purity) and ND_3 (Merck, Sharp and Dohme, 99 atom % D minimum) were used without further purification. H_2 and D_2 (both Matheson CP grade; D_2 99.5 atom % D minimum) were also used without purification.

A.3.3

RESULTS AND DISCUSSION

(a) HF/NH₃ Energy Transfer Measurements

In a previous section, various problems of reproducibility encountered during these experiments were mentioned. In an effort to determine the cause(s) of the observed change in HF vibrational distributions as a function of time, the switching experiment described in the last section was performed. This had as its object the determination of the effect of collisions of HF with a) NH₄F-coated walls and b) NH₃ (in the gas phase) on the measured HF distributions. As the deactivation of HF by NH₃ is very fast⁽⁷³⁾, there has been some speculation regarding the distributions obtained in the low pressure apparatus when ammonia is present⁽³⁾. The results of the switching experiments indicate that, whereas a coating of NH₄F on the reagent inlet walls has a severe effect on the measured distributions, there is no unusual gas phase deactivation process associated with NH₃.

For this experiment, reagent inlet configuration B was used, with the injector withdrawn 7 mm inside tube 2. This ensured that there would be enough wall collisions to provide an adequate test of any effect(s) due to the walls. A continuous flow of SF₆ (3.3 μmol/sec) was discharged in the sidearm of tube 2. H₂ and D₂ flows (3.0 and 4.5 μmol/sec, respectively) were admitted alternately to the injector by way of the four-way stopcock. Various flows of NH₃ (0-5 μmol/sec) were allowed to flow through tube 1.

At the beginning of the experiment, the H₂ and D₂ vibrational

distributions were alternately measured and replicated to provide a base datum. Following this, a small flow of ammonia was added via tube 1 and the second half of the switching experiment carried out. The same sequence of steps was then repeated, but with a slightly higher flow of NH_3 . This procedure ensured that each addition of ammonia to the system was both preceded and succeeded by a run in which both H_2 and D_2 were switched into the injector, with no ammonia flowing. The entire set of measurements was done four times, with increasing amounts of NH_3 introduced each time. The maximum flow of ammonia used for this experiment was $5 \mu\text{mol/sec}$.

The resulting HF vibrational distributions are given in Table A-VIII. (In this and all other tables, the distributions have been normalized such that $\sum_v P_v = 1.0$). The populations for a given run may be compared to those of other runs by multiplying each entry in a line of the table by the value of P_{tot} corresponding to that run. The DF populations showed exactly the same trends as did those of HF; they are excluded from the table for this reason. It should be mentioned, however, that in no case was HF emission observed when only D_2 was flowing in the apparatus (this was called result (b) in the preceding section). This demonstrates that no observable (i.e. vibrationally excited) HF is created in this system by the reaction of F-atoms with NH_3 (or any other species) adsorbed on, or desorbing from, the reagent inlet walls.

The first entry in Table A-VIII (run 14) is the base datum. In each succeeding group of three lines, the entries correspond respectively

Table A-VIII

Results of wall deactivation experiment

RUN	H ₂ FLOW(a)	NH ₃ FLOW(a)	P(v'=1)	P(v'=2)	P(v'=3)	P _{tot}
14	3.0	0.0	.39	.47	.14	1.0
15	0.0	0.2	0.0	0.0	0.0	0.0
16	3.0	0.2	.35	.49	.16	.70
21	3.0	0.0	.35	.48	.17	.70
31	0.0	1.0	0.0	0.0	0.0	0.0
33	3.0	1.0	.28	.55	.17	.45
35	3.0	0.0	.30	.52	.18	.45
36	0.0	3.0	.40	.60	0.0	.15
37	3.0	3.0	.36	.53	.11	.35
39	3.0	0.0	.22	.55	.23	.30
41	0.0	5.0	.42	.58	0.0	.30
42	3.0	5.0	.38	.54	.08	.60
44	3.0	0.0	.21	.56	.23	.30

a) Micromoles/sec.

to the HF distributions from the $F/D_2/NH_3$, $F/H_2/NH_3$ and $F/D_2/H_2$ measurements (results (d), (c), and (a) respectively in the experimental description). The observed HF vibrational distribution from the $F + H_2$ reaction, occurring in the presence of the indicated flow of ammonia, may thus be obtained by subtracting result (d) from (c), after multiplying each by the appropriate P_{tot} .

The results of runs 14, 21, 35, 39 and 44 are the $F + H_2$ results with no ammonia flowing. They show directly the effect on the distributions of the NH_4F deposited during the previous run. From these, it is seen that the observed HF distributions become more inverted and the total intensities diminish as the walls become coated with NH_4F . This is a very large effect; the NH_3 flows in runs 15 and 31 were so small that no emission was detected from the $F + NH_3$ reaction in the $F/D_2/NH_3$ portion of the experiment, but the $F + H_2$ measurements following each showed substantial changes in the distributions (runs 14, 21, 35).

In the interpretation of these results, it is assumed that collisions of vibrationally-excited HF with "clean", teflon-coated walls cause partial vibrational deactivation, whereas collisions with walls contaminated with NH_4F lead to complete vibrational deactivation (to $v' = 0$). Runs 14, 21, 35, 39 and 44 show that there is a decrease in the observed total populations, concurrent with an increase in the degree of inversion. This result may then be interpreted as the removal (to $v = 0$) of molecules which had previously suffered only partial vibrational deactivation on the reagent inlet walls, and had

been observed to emit from the lower vibrational levels. It should be stressed here that the walls referred to in the preceeding discussion are only those of the reagent inlet. No comparable effect (i.e. a change in the HF distributions with time) is observed in this apparatus if the injector is extended substantially below the outer tubes (vide infra). This implies that all vibrationally excited molecules striking the surface of the cooled baffles below the reagent inlet are deactivated to their ground states, before reentering the optical cell.

The same experiment was done using CO_2 instead of NH_3 in tube 1. This served to demonstrate the response of the system to a non-reactive gas, which leaves no wall deposit. Since in this case there was no contribution to the HF or DF intensities due to reaction with the added gas, only the second half of the switching experiment was carried out. The HF and DF distributions were measured alternately while CO_2 was admitted through tube 1. The resulting $\text{F} + \text{H}_2$ distributions are listed in Table A-IX; again, as the $\text{F} + \text{D}_2$ results give the same information, they have been omitted.

There is a great contrast between the results shown in this table and those of the preceeding one. Here, the HF distributions show the "expected" response to an increase in CO_2 flow - the relative populations in lower v-levels increase at the expense of those in higher levels. At the same time, there is a small increase observed in the total emission intensity. The latter is due to the changing flow patterns through the optical cell as the flow of CO_2 is increased. Since some regions of this cell collect light more efficiently than

Table A-IXResults of CO₂ deactivation experiment

RUN	CO ₂ FLOW ^(a)	P(v'=1)	P(v'=2)	P(v'=3)	P _{tot}
43	0	.29	.51	.19	.15
45	1.7	.29	.52	.18	.20
47	15.1	.31	.52	.17	.23
10	56.9	.37	.49	.14	.26

a) Micromoles/sec.

others⁽⁷⁴⁾, changing the flow pattern through it causes a change in the total emission collected.

The important point here, though, is the observation that a noticeable change in the HF vibrational distribution (by more than the estimated accuracy of $\pm 2\%$) occurs only after the CO_2 flow has been increased to more than $20 \mu\text{mol/sec}$. Substantial vibrational deactivation is apparent only when more than $50 \mu\text{mol/sec}$ of CO_2 are flowing. The maximum flow of NH_3 used in the previous experiment was $5 \mu\text{mol/sec}$; the effect on the HF distributions of the addition of much smaller quantities of NH_3 was greater than (and in the opposite sense to) that caused by CO_2 .

The measured distributions for the $\text{F} + \text{H}_2$ runs, listed in Table A-VIII are shown in figure A.3.1. Those resulting from the CO_2 experiment are displayed in figure A.3.2. Comparing the two, the differing behaviour as a result of added gas (NH_3 or CO_2) is illustrated clearly.

These results serve to demonstrate graphically that the deposition, on the walls of the reagent inlet, of solid NH_4F causes drastic and irreversible changes in the measured vibrational distributions of HF. Having knowledge of this effect, great care was taken in all subsequent measurements to eliminate it. After some experimentation, it was determined that when the injector tip was more than about 2.5 cm below the outer tubes, the wall effect no longer influenced the observed results. This is because at this position, the amount of reaction which takes place near the inlet

Figure A.3.1.

HF vibrational populations from the $F+H_2$ reaction, given in Table A-VIII. Run 14 is the base datum; the subsequent runs show the effect of increasing amounts of wall deposit on the measured populations. The increasing degree of inversion and the decreasing total population as a result of this deposit are obvious.

Figure A.3.2.

HF vibrational populations from the $F+H_2$ reaction, given in Table A-IX, occurring in the presence of increasing amounts of CO_2 . Run 43 represents the lowest CO_2 flow; run 10, the highest. The "normal" deactivation of HF by CO_2 is clearly seen.

glassware is insignificant.

(b) Effect of Reagent Flows on Observed Distribution

In the following, it will be demonstrated that the measured HF and DF vibrational distributions in the F/NH_3 (ND_3) system behave in a straightforward and reproducible manner as a function of reagent flows (SF_6 and NH_3). It will be argued that the only self-consistent interpretation of the resulting data lies in the following conclusions: 1) The vibrational distribution of the product HF from the primary reaction [2] is a cold (non-inverted) one, and 2) The secondary, radical reaction [1], is faster than the primary reaction and gives rise to substantial inversion in the product HF vibrational distribution.

(i) Effect of Molecular Reagent Flow

The responses of the vibrational distributions and total populations to changes in the NH_3 flow and injector location were explored in an experiment in which the NH_3 was introduced via the injector and F-atoms were flowing through tube 2. In view of the results presented immediately above, it is important to note the order in which the data was taken. First, several measurements were made with the injector withdrawn inside tube 2. This had the effect of partially coating the inlet glassware with NH_4F . The experiments listed in Table X-X were then carried out. Their chronological order followed the numbering in the table.

The results given in this table illustrate several points. It should first be noted that all the experiments were done with the

Table A-X

F/NH₃ results for different conditions

RUN	Injector Location ^(b)	SF ₆ FLOW ^(a)	NH ₃ FLOW ^(a)	P(v'=1)	P(v'=2)	P(v'=3)	P(v'=4)	p _{tot}
26	-0.5	6.0	2.5	.43	.51	.03	.02	.12
27	-1.0	7.2	3.3	.43	.51	.04	.02	.20
28	-2.0	6.8	3.0	.45	.50	.03	.02	.16
29	-3.0	3.9	3.0	.53	.45	.02	-	.16
30	-3.0	1.7	3.0	.62	.37	.01	-	.06
31	-3.0	3.9	3.0	.54	.44	.02	-	.16
32	-3.0	3.9	8.5	.53	.46	.01	-	.33

a) Micromoles/sec.

b) cm. Negative values indicate locations below the end of Tube 2.

injector outside the outer tubes (reagent inlet configuration A was used for these runs). The first three runs show the effect of successively lowering the injector still farther outside tubes 1 and 2, while maintaining approximately constant reagent flows. This has the effect of reducing the density of F-atoms in the reaction zone, but keeping the pressure, flow and pumping speed in the apparatus constant. These three runs (26, 27, 28) demonstrate that the measured HF vibrational distribution does not change much upon decreasing the reagent density, over the range shown. It should be pointed out, however, that all three runs had fairly high flows of SF_6 (and thus F-atom density), all show an inversion in the $v' = 2/v' = 1$ ratio and all show some (small) population in $v' = 4$. As the latter level is thermochemically inaccessible to reaction [2], the observed emission indicates that the radical reaction was contributing to some extent to the observed distributions. In fact, for all experiments reported herein, if the conditions involved either a high flow of F-atoms or an injector position close to the ends of the outer tubes, both an inversion in the HF $v' = 2/v' = 1$ ratio and measurable emission from the $v' = 4$ level were seen.

The next entry (Run 29) shows that when the injector is extended still farther outside the outer two tubes and the flow of F-atoms decreased, the inversion in the $v' = 2/v' = 1$ ratio disappears and no emission is observed from $v' = 4$. Run 30 represents the lowest flow of F-atoms which could be used, while retaining a useful signal-to-noise ratio, at this injector location. It is seen that the $v' = 2/v' = 1$ ratio continues to decrease with decreasing F-atom

flow. The following run (31) is a check on run 29. It shows that, at the reagent flows and injector location listed, there is no observable wall effect (i.e., the measured distributions are reproducible after the passage of some time).

Run 32 shows that increasing the flow of ammonia from 3.0 to 8.9 $\mu\text{mol/sec}$ has no effect (outside the experimental error of $\pm 2\%$) on the distribution, though it does increase the total population, as expected. A further increase in the ammonia flow was not attempted for two reasons. First, it was desired to reduce the wall effect as much as possible; at very high flows of NH_3 substantial deposits of NH_4F were observed to form on the inlet glassware, even at low injector positions. This deposit also formed on the optical cell mirrors, especially when the injector was at its lowest position. Thus the flow range of these experiments was somewhat curtailed.

The last three runs (30, 31, and 32) illustrate clearly that the observed distribution is quite sensitive to the flow of F-atoms, but not to that of NH_3 .

The interpretation of this observation is made easier by a simple estimation of the steady-state concentration of NH_2 radicals in the reaction zone. If the rate of creation (via reaction 2) is set equal to the rate of loss via diffusion out of the reaction zone, the following expression is obtained:

$$[\text{NH}_2]/[\text{NH}_3] = [\text{F}] \times k_{\text{rxn}}/k_{\text{loss}} \quad [3]$$

In equation [3], $k_{(\text{rxn})}$ is the rate constant for reaction [2] ($0.39\text{--}1.0 \times 10^{-10}$ cc/molec/sec^(3,71); $1.36\text{--}3.56 \times 10^6$ Torr⁻¹sec⁻¹) and $k_{(\text{loss})}$ is the rate constant for diffusion out of the reaction

zone. If the characteristic length of this zone is taken as 1 cm and a near free-molecular velocity (1×10^4 cm/sec) assumed for the NH_2 , the rate constant ratio in [3] becomes about 100 Torr^{-1} .

An estimate as to the density of F-atoms in the reaction zone can also be made. Assuming a 33% conversion of SF_6 to F-atoms and the measured flow of SF_6 from run 26, the flux of F-atoms at the bottom of tube 2 becomes about $1.5 \times 10^{18} \text{ cm}^{-2} \text{ sec}^{-1}$. If it is further assumed that the average velocity at this point is 1×10^4 cm/sec, the corresponding pressure of F-atoms becomes $4 \times 10^{-3} \text{ Torr}$. As the F-atoms expand out of tube 2, this pressure drops slowly, due to the collimating effect of long tubes on low pressure flows⁽⁷⁵⁾. Recalling that the rate constant ratio in [3] is about 100 Torr^{-1} , the ratio of radical to molecule concentration becomes on the order of 0.1 in the region immediately beneath the reagent-inlet glassware.

This simple analysis serves to illustrate two points. First, equation [3] shows that the concentration ratio: $[\text{NH}_2]/[\text{NH}_3]$ is primarily dependent upon the F-atom concentration and not strongly influenced by the NH_3 concentration. Since the rate of the radical reaction is faster than that of the primary reaction⁽⁷⁶⁾, it is this ratio which determines the contribution of the secondary reaction to the measured distributions. This contribution is thus predicted to increase with increasing F-atom flow, but not to change with varying NH_3 flow. This is what is seen experimentally. Runs 31 and 32 of Table A-X give almost identical distributions, in spite of a three-fold increase in NH_3 flow. Decreasing the F-atom flow by a factor

of two, however, results in a substantial change in the HF vibrational distribution. It becomes colder for the lower F-atom flow - conditions under which the contribution to the observed distribution from the atom/radical reaction [1] is expected to decrease.

The vibrational populations for runs 30, 31 and 32 are illustrated in Figure A.3.3. The increase in inversion with increasing F-atom flow, the increase in total intensity with increasing reagent flows and the insensitivity of the distribution to an increase in NH_3 flow are all clearly displayed.

The same experiment was carried out for the F/ND_3 system. The results are listed in Table A.XI and illustrated in Figure A.3.4. Once again, reagent inlet configuration A was used; the injector was kept at 3 cm below the outer tubes.

In this case, a "V-shaped" vibrational distribution for the product DF was obtained. It is not possible, based on the results given in the table, to determine whether this is the correct, nascent distribution, or whether an isotope effect ~~does~~ exist for this reaction⁽¹⁷⁾. Regarding this, however, it should be noted that the flow of F-atoms required to provide an adequate signal-to-noise ratio in the case of $\text{F} + \text{ND}_3$ was higher than that necessary for $\text{F} + \text{NH}_3$. This is due to the fact that the Einstein transition probabilities for DF are lower than those of HF. It was observed that the degree of inversion in the $\text{F} + \text{NH}_3$ results increased with increasing F-atoms flows due to contributions from the secondary reaction. The $v' = 3/v' = 2$ inversion seen here for the $\text{F} + \text{ND}_3$ system may also be due to contributions from secondary reactions.

Figure A.3.3.

HF vibrational populations from the F/NH₃ system, with the injector at its lowest position, as reagent flows are increased. The results shown are those of Table A-X. Run 30 represents the lowest flow conditions; run 32, the highest.

Table A-XIF/ND₃ results for different ND₃ flows

RUN	SF ₆ FLOW(a)	ND ₃ FLOW(a)	P(v'=1)	P(v'=2)	P(v'=3)	P(v'=4)	P _{tot}
23	4.6	0.6	.31	.29	.40	-	.11
24	4.6	4.3	.33	.30	.37	-	.23
25	4.6	7.9	.31	.30	.39	-	.32

a) Micromoles/sec.ē

Figure A.3.4.

DF vibrational populations from the F/ND₃ system, with the injector at its lowest position, as the ND₃ flow is increased. The results are those of Table A-XI. Run 23 represents the lowest ND₃ flow; run 25, the highest.

This point is addressed more fully below.

(ii) Effect of F-Atom Flow

In order to explore fully the effect of the F-atom concentration on the measured distributions, an experiment very similar to that used to identify the wall effect was performed. In this experiment, NH_3 and H_2 were alternately switched into the injector and F-atoms flowed through tube 1. For some of the runs a constant flow of D_2 was admitted into tube 2. The flows of NH_3 , H_2 and D_2 were kept constant; they were, respectively, 2.7, 3.0 and 5.6 $\mu\text{mol/sec}$. The SF_6 flow, from which the F-atom flow was derived, was varied from less than 0.5 to more than 17 $\mu\text{mol/sec}$. The injector tip was maintained at 2 cm below the outer tubes (using inlet configuration A).

This arrangement provided several checks on the stability and self-consistency of the measured distributions. Switching the NH_3 and H_2 flows into the injector provided a test for the reproducibility of the data as a function of time (and thus, added ammonia). As an F + H_2 measurement was carried out after each F + NH_3 run, any wall effects occurring under these conditions could be observed. D_2 was flowing at all times during the latter part of the experiment; the resulting F + D_2 distributions gave information about any relaxation effects which might have been present in the F/ NH_3 system but absent for F/ H_2 .

In the experiment, no difference in the measured DF vibrational distribution was observed (outside experimental error) whether

NH_3 or H_2 was flowing. Table A-XII reports the DF vibrational distributions for the $\text{F} + \text{D}_2$ portion of this experiment. Two widely varying F-atom flows are shown; in the lower flow runs, the signal-to-noise ratios in the DF spectra were too low to assign a population to $v' = 1$. At the higher flow, there was sufficient signal from $v' = 1$ of DF to assign a population to that level. The latter results appear to be somewhat vibrationally relaxed over those corresponding to the lower flow. Note, however, that there is no difference (outside experimental error) between the distributions measured in each case whether NH_3 or H_2 was flowing.

Table A-XIII and Figure A.3.5 show the effect on the HF vibrational populations of increasing the F-atom flow in the NH_3 half of the experiment. The trend in the data is obvious; with increasing F-atom flow, the measured distribution becomes more excited and the total population increases. For the two highest flows, emission is recorded from $v' = 4$ -energetically forbidden to the F/NH_3 reaction, but accessible to reaction [1]. The amount of inversion in the $v' = 2/v' = 1$ ratio increases with increasing intensity in the $v' = 4$ population. In the present case, because of the injector location (2 cm. below both outer tubes), the F-atom density is too large in the reaction zone to completely eliminate contributions from the secondary reaction. At the lowest flow of F-atoms used in this experiment, the observed distribution is still more excited than that seen when the injector is even further extended (cf. run 30 of Table A-X).

The $\text{F} + \text{H}_2$ distributions, recorded alternately with those of

Table A-XIIDF results in $F+NH_3/H_2$ switching experiment

Run	SF ₆	H ₂	NH ₃	P(v'=1)	P(v'=2)	P(v'=3)	P(v'=4)
22	1.0	-	5.3	-	.15	.49	.36
23	1.0	6.0	-	-	.15	.52	.32
20	47.8	-	5.3	.06	.25	.44	.25
21	47.8	6.0	-	.05	.23	.45	.26

Table A-XIIIF/NH₃ results from F+NH₃/H₂ switching experiment

RUN	SF ₆ FLOW(a)	NH ₃ FLOW(a)	P(v'=1)	P(v'=2)	P(v'=3)	Pv'=4)	P _{tot}
42	.43	2.7	.52	.48	.01	-	.01
38	2.9	2.7	.51	.47	.02	-	.06
40	6.5	2.7	.45	.51	.03	.01	.11
44	17.4	2.7	.39	.54	.05	.02	.28

a) Micromoles/sec.

Figure A.3.5.

HF vibrational populations from the F/NH₃ portion of the NH₃/H₂ switching experiment, given in Table A-XIII. The data show the effect of increasing the F-atom flow. Run 42 is the lowest flow; run 44, the highest. The increasing degree of inversion and total population, as well as the observation of $v'=4$, as the F-atom concentration is increased are obvious.

$F + NH_3$, are shown in Table A-XIV and Figure A.3.6. The run numbers indicate the chronology of these runs with respect to the $F + NH_3$ runs. The trend in the measured distributions observed here is opposite to that seen for the $F + NH_3$ case. A very slight deactivation of the measured distribution is apparent at the highest F-atom flows. This deactivation is in the expected, "normal" sense: the populations of the lower vibrational levels increase, at the expense of those of the higher levels. The emission intensity increases with the flow, as expected.

The complementary experiment, switching ND_3 and D_2 in the injector, was also performed. Inlet configuration A was again used; the injector was kept 2.5 cm below the outer tubes. For this experiment, H_2 flowed continuously in tube 1; F-atoms were introduced via tube 2. The flows of ND_3 , D_2 and H_2 were, respectively, 1.0, 4.1 and 2.8 $\mu\text{mol/sec}$. Once again, the measured $F + H_2$ distributions were insensitive (to within the experimental error) to the reagent flowing in the injector. These are shown in Table A-XV. Some deactivation of the HF is apparent as the F-atom flow is increased. However, for each pair of runs (ND_3 , D_2), the observed HF distribution is the same.

The results of the $F + ND_3$ half of this experiment are shown in Table A-XVI and Figure A.3.7. At the lowest flow of F-atoms, the "V-shaped" distribution is again seen. As the F-atom flow is increased, the measured distribution becomes increasingly excited. At the highest flows of F-atoms recorded here, the DF vibrational distribution is almost identical to the one reported by Manocha et al.

Table A-XIVF/H₂ results from F+NH₃/H₂ switching experiment

RUN	SF ₆ FLOW(a)	H ₂ FLOW(a)	P(v'=1)	P(v'=2)	P(v'=3)	P _{tot.}
43	.43	3.0	.15	.57	.28	.01
39	2.9	3.0	.16	.56	.28	.06
41	6.5	3.0	.17	.56	.27	.13
45	17.4	3.0	.18	.56	.26	.25

a) Micromoles/sec.

Figure A.3.6.

HF vibrational populations from the F/H₂ portion of the NH₃/H₂ switching experiment, given in Table A-XIV. The effect of increasing the F-atom flow in this case is very different from that shown in the previous figure, for the F/NH₃ system. Run 43 represents the lowest flow; run 45, the highest.

Table A-XVF/H₂ results from F+ND₃/D₂ switching experiments

RUN	SF ₆	D ₂	ND ₃	P(v'=1)	P(v'=2)	P(v'=3)
29	2.3	-	1.0	.18	.56	.26
30	2.3	4.1	-	.19	.55	.26
31	4.6	4.1	-	.22	.54	.23
32	4.6	-	1.0	.22	.54	.24
33	11.5	4.1	-	.25	.54	.21
34	11.5	-	1.0	.25	.53	.22
35	19.0	4.1	-	.25	.54	.22
36	19.0	-	1.0	.25	.53	.22
37	33.5	4.1	-	.25	.54	.21
38	33.5	-	1.0	.25	.53	.21

Table A-XVIF/ND₃ results from F+ND₃/D₂ switching experiment

RUN	SF ₆ FLOW(a)	ND ₃ FLOW(a)	P(v'=1)	P(v'=2)	P(v'=3)	P(v'=4)	P _{tot}
29	2.3	1.0	.36	.27	.37	-	.06
32	4.6	1.0	.29	.30	.41	-	.22
34	11.5	1.0	.18	.35	.46	-	.68
36	19.0	1.0	.17	.35	.48	-	.92
38	33.5	1.0	.15	.37	.48	-	1.36

a) Micromoles/sec.

Figure A.3.7.

DF vibrational populations from the F/ND_3 portion of the ND_3/D_2 switching experiment, given in Table A-XVI. The results show the effect of increasing the F-atom flow on this system. Run 29 represents the lowest F-atom flow; run 38, the highest. As for F/NH_3 , an increase in inversion and total population are the results of increasing the F-atom concentration.

(3) in a fast-flowing afterglow apparatus, and ascribed entirely to the $F + ND_3$ primary reaction. Figure A.3.7 shows that, as the flow of F-atoms increases, the populations of v-levels 2 and 3 rise faster than that of $v = 1$. If this trend is extrapolated backwards to zero F-atom flow, it predicts that the $v' = 2$ and 3 populations should decrease faster than that of $v' = 1$ as the F-atom flow is decreased - thus indicating a cold, non-inverted vibrational distribution for the $F + ND_3$ reaction. This latter would then be very similar to that observed in the $F + NH_3$ case. However, because the populations of the various v-levels evolve in a non-linear fashion as a function of F-atom flow, a quantitative extrapolation to extract the nascent vibrational distribution is not warranted.

The results for the $F + D_2$ half of this experiment are displayed in Table A-XVII and Figure A.3.8. As for the comparison of the F/NH_3 and F/H_2 systems discussed above, these data show the opposite trend with increasing F-atom flow to those of the $F + ND_3$ portion of the experiment. The distributions show some evidence of vibrational deactivation as the SF_6 flow is increased; they also show the expected increase in total population. The deactivation is again in the expected sense; the population of the highest level ($v' = 4$) decreases somewhat and those of $v' = 2, 3$ increase.

(c) Summary of Experimental Results

In the foregoing, it has been demonstrated that:

- 1) Reagent inlet walls which have been coated with NH_4F give rise to a decrease in the total emission intensity and an apparent

Table A-XVIIF/D₂ results from F+ND₃/D₂ switching experiment

RUN	SF ₆ FLOW(a)	D ₂ FLOW(a)	P(v'=1)	P(v'=2)	P(v'=3)	P(v'=4)	P _{tot}
30	2.3	4.1	-	.19	.47	.34	.09
31	4.6	4.1	.07	.19	.43	.31	.24
33	11.5	4.1	.08	.20	.46	.26	.86
35	19.0	4.1	.06	.24	.43	.27	1.41
37	33.5	4.1	.06	.21	.46	.27	1.90

a). Micromoles/sec.

Figure A.3.8.

DF vibrational populations from the F/D_2 portion of the ND_3/D_2 switching experiment, given in Table A-XVII. Run 30 represents the lowest F-atom flow, run 37, the highest. The contrasting behaviour between these results and those of the previous figure is obvious.

increase in the vibrational excitation in the $F + H_2$ system. The magnitude of these effects increases with the amount of NH_3 introduced to the apparatus (and hence NH_4F deposited on the walls of the inlet). Only experiments in which the wall effect is absent give reproducible measured distributions in the present apparatus.

2) Under conditions such that the wall effect is not observed, the product HF vibrational distribution in the F/NH_3 system is very sensitive to F-atom flow, but insensitive to NH_3 flow, over the range of flows described herein.

3) Under conditions in which the ratio of $[NH_2]/[NH_3]$ is low (i.e. low F-atom densities) the observed product vibrational distribution is non-inverted for F/NH_3 and "v-shaped" for F/ND_3 . In the case of the latter, it is probable that the ratio of radical to molecular concentration was higher than for F/NH_3 , due to the higher F-atom flows used. As this ratio determines the contribution of the secondary reaction to the total product density, it is concluded that the cold vibrational distribution is the initial one. This cold distribution does not change when the NH_3 concentration is increased over a wide range.

4) When the contribution from the secondary reaction to the observed distribution is increased by increasing the flow of F-atoms, the initially cold vibrational distribution becomes inverted. Concurrent with the observation of inversion in the $v' = 2/v' = 1$ ratio of HF is the observation of emission from $v' = 4$ of that molecule. This level is only energetically accessible to the secondary reaction.

The intensity of the $v' = 4$ emission and the degree of inversion in $v' = 2/v' = 1$ both increase as the F-atom flow is increased. The same effect (increasing inversion with increasing F-atom flow) is obtained in the F/ND₃ system.

The only self-consistent interpretation which can be drawn from these observations is the following:

- 1) The initial HF(DF) vibrational distribution from the F + NH₃ (ND₃) reaction is non-inverted. The derived initial distributions are given in Table A-XVIII. In the case of F + ND₃, the distribution shown is possibly not the nascent one; it probably still shows some contribution from the secondary reaction.
- 2) The HF(DF) vibrational distributions arising from the F + NH₂(ND₂) reaction must be inverted, peaking strongly in $v' = 2$, in the case of HF and $v' = 3$, for DF. The profound effect that these secondary reactions have on the observed product energy distributions implies that the secondary reactions are faster than the primary reactions⁽⁷⁶⁾.

(d) Dynamical Interpretation

(i) The Primary Reaction

The results presented in the previous sections indicate that the primary reaction:—

gives rise to a cold vibrational distribution in the HF product ($v' = 1/v' = 2$) ratio of 0.6/0.4), while the secondary, radical reaction:

Table A-XVIIIHF(DF) vibrational distribution from $F+NH_3(ND_3)$

REACTION	DISTRIBUTION		
	$P(v'=1)$	$P(v'=2)$	$P(v'=3)$
$F + NH_3 \rightarrow HF(v') + NH_2$	0.60	0.40	-
$F + ND_3 \rightarrow DF(v') + ND_2$	0.36	0.27	0.37

produces HF which is vibrationally excited, with a strong inversion in the $v' = 2/v' = 1$ ratio. This conclusion is somewhat contrary to expectation; as discussed previously in this work and elsewhere⁽⁴⁾ the abstraction of a hydrogen atom from an R-H molecule by a fluorine atom usually gives rise to an inverted vibrational distribution in the HF product, with population of the product levels up to the thermochemical limit.

Some recent reports from this laboratory^(15,16,18,19), however, have indicated that this is not always the case. The HF(DF) vibrational distributions for the reactions:

are found to decrease monotonically with v-level. This has been interpreted as being the result of partial energy randomization in the nascent HF(DF) product due to the formation of an intermediate F-H-R complex. (Here R represents the radical product of the abstraction reaction.) In the case of reactions [4], above, it was found that a partial phase-space calculation (similar to the one detailed in the last chapter, but including only some of the radical

product modes in the phase space) gave predicted vibrational distributions which were in good agreement with those observed experimentally⁽¹⁹⁾. Semi-empirical calculations⁽¹⁵⁾ of the F/HN₃ system indicated that minima exist in the potential energy surface as the F-atom approaches the HN₃ molecule. The decomposition of the complex thus formed was believed responsible for the observed HF distribution.

In conjunction with the experimental work on the F/NH₃ system, discussed in the previous sections, ab-initio calculations were performed by Goddard⁽⁷⁷⁾ on the reaction. The results of these calculations, to be discussed in the following paragraphs, provide a very clear interpretation of the experimental results. A strong hydrogen bond was found to exist between the departing HF and NH₂ fragments. As in the case of the FHCO complex, the frequency corresponding to the HF stretch in the FHNH₂ complex thus formed is predicted to be considerably smaller than that of the free molecule. This decrease (associated with hydrogen bond formation) brings the HF frequency into near resonance with the mode in the complex which ultimately evolves into the NH₂ asymmetric stretch. Thus energy which is initially deposited into HF vibration can, in the exit channel, be lost to the NH₂ via this near resonance.

The calculations were carried out at the SCF level, using both the 4-31G⁽⁷⁸⁾ and 6-311G**⁽⁷⁹⁾ basis sets of Pople and coworkers. Geometry optimizations were performed, using both basis sets, for the species NH₃, HF, NH₂ and the FHNH₂ intermediate complex. Harmonic vibrational frequencies were also calculated for the latter three

species using both basis sets. Tables A-XIX and A-XX list respectively, the optimized geometries and harmonic frequencies obtained and, for comparison, the experimental values (where these are known).

Both levels of calculation predict that the $(F \cdots H \cdots NH_2)$ complex is bound with respect to products HF and NH_3 , with a binding energy of 14 kcal/mol for the 4-31G basis set and 9.7 kcal/mol for the larger one. These values are in good accord with what might be expected of an $HF \cdots NH_3$ hydrogen bond. Ab-initio calculations of the hydrogen bond strength in $FH \cdots NH_3$ have yielded values of 11.67 (80) and 10.1 (81) kcal/mol. The $ClH \cdots NH_3$ hydrogen bond has been studied both theoretically (82,83) and experimentally (84); the measured and predicted bond energies are in good agreement, at about 10 kcal/mol. For the $H_2O \cdots HF$ complex, Thomas (85) determined experimentally a value of 7 ± 1.5 kcal/mol for the hydrogen bond strength.

The $FHNH_2$ complex is predicted to have C_{2v} symmetry with the geometry given in Table A-XIX. At both levels of calculation, it is seen that the properties (bond lengths and angles) of the two partners in the hydrogen bond are very close to those calculated for the separated fragments. The 4-31G calculation yields bond lengths for HF and NH_3 in somewhat better agreement with experiment than the 6-311G** values. In particular, the HF bondlength is only 0.005 Å different from experiment, while that predicted by the larger basis set is 0.021 Å too short. The bond angles predicted by the 4-31G basis set are not as good as those of the 6-311G**, however.

Table A-XIX

Geometry calculations for HF...NH₂ complex

Species	Parameter ^(a)	Basis set		
		4-31G	6-311G**	exp't
HF	r_e	0.922	0.896	0.917 ^(b)
NH ₂	$r_e(\text{NH})$	1.015	1.012	1.024
	$\theta(\text{HNH})$	108.3	104.0	103.5 ^(c)
NH ₃	$r_e(\text{NH})$	0.991	1.001	1.012
	$\theta(\text{HNH})$	115.8	107.4	106.7 ^(d)
FH...NH ₂	$r_e(\text{NH})$	1.010	1.009	
	$\theta(\text{HNH})$	110.6	106.2	
	$r_e(\text{HF})$	0.942	0.909	
	$r_e(\text{H...N})$	1.772	1.883	

a) bond lengths in Å, angles in degrees

b) ref. 29

c) ref. 86

d) ref. 87

Table A-XX

Calculated vibrational frequencies for both basis sets

Species	Vibration ^(a)	Frequency ^(b)		
		4-31G	6-311G**	exp't
HF	$\omega_1(a_1)$	4121	4514	4138 ^(c)
NH ₂	$\omega_1(a_1)$ sym.str.	3527	3597	3219 ^(d)
	$\omega_1(a_1)$ bend	1659	1645	1497 ^(c)
	$\omega_3(b_1)$ asym.str.	3644	3684	3280 ^(d)
FH...NH ₂	$\omega_1(a_1)$ FH str.	3705	4207	
	$\omega_2(a_1)$ NH ₂ sym.str.	3596	3636	
	$\omega_3(a_1)$ NH ₂ bend	1665	1648	
	$\omega_4(a_1)$ F..H..N str.	274	221	
	$\omega_5(b_1)$ NH ₂ asym.str.	3719	3730	
	$\omega_6(b_1)$	900	785	
	$\omega_7(b_1)$	230	236	
	$\omega_8(b_1)$	876	762	
	$\omega_9(b_2)$	354	296	

a) ~~C_{2v}~~ symmetryb) all frequencies in cm⁻¹

c) ref. 29

d) ref. 88

e) ref. 88a

Table A-XX presents the predicted harmonic vibrational frequencies for the complex and two product fragments. These frequencies are labelled with their symmetry-group representation (in C_{2v}); some are also given a qualitative descriptive label (i.e. FH stretch). The isolated HF frequency given by the 4-31G basis set is in excellent accord with experiment. In contrast, the 6-311G** predicted HF frequency is some 400 cm^{-1} higher than experiment; the predicted bond length was also too short. Since the value of the HF frequency is of paramount importance to the energy partitioning discussion to follow, the 4-31G predictions for the complex vibrational frequencies are to be preferred over those of the 6-311G** basis set.

The modes of the complex which do not correlate to translation and rotation in the products are seen to be very similar to those of the isolated products, except for that corresponding to HF. This frequency, in the environment of the complex, is considerably lower than that of the free HF in both levels of calculation. The 4-31G result, which is preferred for reasons given above, shows that in the complex, the HF frequency is reduced to about 3700 cm^{-1} , from 4121 cm^{-1} in the isolated molecule. This reduction of some 400 cm^{-1} brings it into near resonance with two other modes in the complex: those correlating to the symmetric and antisymmetric stretch of NH_2 .

This decrease in HF vibrational frequency associated with hydrogen-bond formation is to be expected. Many studies, both experimental (84-88) and theoretical (82,88a) on hydrogen-bonded

HX systems have shown that the HX frequency decreases by some hundreds of wave numbers in the hydrogen-bonded complex. In particular, Thomas (84.) observed the H-F stretch in the $\text{FH}\cdots\text{OH}_2$ complex to be $3608 \pm 2 \text{ cm}^{-1}$ - a decrease of some 500 cm^{-1} from that of free HF. Ab-initio calculations (88a) on the same system yielded a value of ~~3599~~ 3599 cm^{-1} for the (anharmonic) HF frequency in the complex, representing a decrease of 432 cm^{-1} from that predicted for the isolated molecule. Raffenetti and Phillips⁽⁸²⁾, in another ab-initio work, predicted a frequency of 2550 cm^{-1} for the H-Cl stretch in $\text{ClH}\cdots\text{NH}_3$. The experimental value for isolated HCl is 2854 cm^{-1} . The present result is thus entirely consistent with what is currently known about these systems.

The dynamical implications of the results described above are significant. Reaction [2] has an exoergicity of 29 kcal/mol ; a potential energy well of some 10 kcal/mol in the exit channel thus represents a major feature on the reactive surface. The nascent HF, perhaps initially formed with substantial vibrational excitation, is not free of the influence of its co-product, NH_2 . The presence of the potential well in the exit channel has the effect of keeping the nascent products in close proximity for some time after the initial encounter. Energy initially deposited into HF vibration is thereby enabled to escape from the HF to other modes of the complex thus formed. Near resonances between the HF frequency in the complex and those involving NH stretches will facilitate this process. The HF molecule ultimately formed would be expected to be vibrationally cold.

(ii) The Secondary Reaction

The conclusion drawn from the experimental results presented above, for the F/NH₃ system, was that the radical reaction:

and its isotopic analogue give rise to a strongly inverted vibrational distribution in the product HF. This result is not that expected for an atom/radical system which can pass through an intermediate configuration corresponding to a strongly-bound molecule. As mentioned previously, the dynamics of these reactions are often strongly influenced by the presence of such a deep potential energy well. These potential wells often have the effect of removing any specificity from the product energy disposal. The observed product vibrational distributions thus become monotonically-decreasing with v-level, as was the case in the F/HCO system. This is clearly not the case for reaction [1]. Qualitatively, vibrational energy appears to be partitioned very specifically into v' = 2 of the HF product.

A schematic correlation diagram for the F/NH₂ system is shown in Figure A.3.9. In C_s symmetry, there is only one potential energy surface directly correlating ground state reactants and products - the ³A". Another surface (in C_s symmetry) may be traversed by the reacting system. This surface, (¹A') correlates ground state reactants to the bound molecule FNH₂. The latter does not correlate to ground state products, but to the first electronically-excited state of NH - NH (a¹Δ). Both electronic states of NH are energetically accessible to the reaction, but if the NH is formed in the ¹Δ state,

Figure A.3.9.

Schematic correlation diagram, in C_s symmetry, for the $F+NH_2 \rightarrow HF+NH$ reaction. The $^3A''$ surface is the only one directly connecting ground state reactants and products. The transition state geometry on this surface is that calculated by Goddard (77).

not enough energy remains to give even one quantum of vibration in HF. Hence the HF product seen in this work must come from reactions in which the NH is formed in its ground $^3\Sigma^-$ state.

Recent results from this laboratory on the systems F/OH (10), which is isoelectronic with F/NH₂, and F/HNF (9,23), which is analogous to it, have indicated that the surface connecting ground state reactants and products is not the only one upon which reaction can take place. For those systems, it was argued on the basis of the observed HF energy distributions that reaction took place via a surface crossing mechanism. According to this argument, the reaction started on the singlet surface correlating to the bound molecules FOH or HNF₂, but, somewhere in the exit channel, a surface switch took place and the reaction produced ground state products. An ab-initio calculation (9) of the barrier height on the lowest triplet surface (which correlated directly to products) demonstrated that in the F/OH system, this surface switching mechanism was the only possible route to products. The calculated barrier height (ca. 12 kcal/mol) was too high to be overcome by thermal reagents. In the case of F/HNF such a calculation was not undertaken, but the observed HF vibrational distribution was well fitted by a statistical calculation, similar to the one previously described herein. The conclusion was that the reaction passed through a bound HNF₂ complex which underwent a unimolecular decomposition, producing the observed monotonically-decreasing HF distribution.

The present results indicate that for the F/NH₂ system, such is

not the case. The degree of specificity in the observed product energy disposal precludes its being the result of any energy randomization process. This implies that the reaction does not proceed via a long-lived FNH_2 complex. Two possibilities remain: 1) The reaction proceeds upon the $^1\text{A}'$ surface, but that vibrational excitation in the NH_2 reactant gives rise to specific energy disposal in the HF product. 2) The reaction occurs via a direct abstraction on the $^3\text{A}''$ surface. The NH_2 reactant may or may not be vibrationally excited.

The first possibility is very unlikely. In order that both HF ($v' = 4$) and $\text{NH}(^1\Delta)$ be formed, some 34 kcal/mol of excess energy (corresponding to ca. 3 quanta in the NH stretches) must be brought to the reaction by the NH_2 reagent. This energy must then be partitioned specifically into HF vibration. This amount of energy corresponds to only about half of the chemical energy released by the formation of the $\text{H}_2\text{N-F}$ bond. It is likely that the presence of the deep potential well will still dominate the outcome of the reaction under these circumstances. Recent work in this laboratory on the F/OH ($v = 1-4; 7-9$) system ⁽¹³⁾ shows no specificity of energy disposal in the HF product. The potential minimum in this case was only ca 60 kcal/mol below ground-state reagents; the OH ($v = 7-9$) possessed more than this amount of energy in vibration. Thus in the present case, it is felt that vibrational excitation in the NH_2 reagent is not likely to give rise to specific energy disposal in the HF product. This argument suggests that reaction [1] occurs on the $^3\text{A}''$ surface.

Preliminary calculations, also carried out by Goddard⁽⁷⁷⁾, indicate that the barrier to reaction on the $^3A''$ surface is small - certainly less than 10 kcal/mol. and perhaps non-existent. This low barrier height means that the F/NH₂ system, unlike the F/OH system, is not constrained to react on the $^1A'$ surface. A direct abstraction of the hydrogen atom then becomes possible. This mechanism would be expected to produce an inverted vibrational distribution in the HF product, as is commonly observed in abstraction reactions involving F-atoms and molecules⁽⁴⁾. In this case, any vibrational excitation brought to the reaction by the NH₂ would be expected to increase the specificity of the product energy disposal. Many studies have been done investigating the effect of reagent vibrational energy on observed product distributions for several three-atom systems^(7,89-91). These studies have shown that quite often $\langle V \rangle \rightarrow \langle V' \rangle$, i.e. excess reagent vibrational energy is translated into vibrational energy in the products. If the same idea holds true for this four-atomic system, it might help to explain the seeming preference of reaction [1] to populate HF ($v' = 2$).

(e) Energy Distribution from Reaction (1)

An attempt was made to deconvolute the contributions from the primary:

and secondary:

reactions to the measured HF vibrational distributions. The method used to do this made use of a computer program specifically written to model the present apparatus. This numerical simulation (hereinafter referred to as "the simulator") is described in some detail in Appendix 2. A brief summary of its important features is presented here.

The major aspect of the simulator is a numerical integration of all rate processes contributing to the observed population in each energetically-accessible vibrational state of HF. These processes include formation by chemical reaction, energy transfer (both in the gas phase and on the inlet walls), spontaneous emission and diffusion out of the optical cell. Published values of detailed rate constants for primary chemical reactions⁽⁷¹⁾ and energy-transfer processes⁽⁷³⁾ were used. Six variable parameters were used to describe experimentally unobtainable aspects of the apparatus. Three of these described wall deactivation of HF^+ , one gave the average number of F-atoms produced in the microwave discharge per precursor molecule and the last two described the rate of expansion of gases leaving the inlet and the rate at which these approached their free molecular velocities.

These six parameters were optimized, using a "calibration reaction" $\text{F} + \text{H}_2$, for which all other rate processes are well established^(71,73). Eleven experimental measurements of that reaction (which incorporate the relative populations in $v' = 1-3$ of HF and the total emission intensity) yielded forty-four data

values which must be reproduced by the calculation. The six parameters were optimized on these data by a multi-dimensional optimization technique. The resulting predicted HF distributions were within the range of the $\pm 2\%$ experimental error; the total intensities were reproduced to within $\pm 10\%$. These results are shown in Table A-XXI. Both the predicted and measured vibrational distributions and relative total intensities are given, for comparison.

After extensive experimentation with the simulator, optimum values of the parameters and the amounts by which they could be varied, while still reproducing the measured data, were obtained. (A full sensitivity analysis was carried out for each parameter in the numerical model.) Armed with this information, the HF vibrational distribution from reaction [1] was extracted from the measured distributions.

The data given in Tables A-XIII and A-XIV was used in the simulation. The wall deactivation parameters were first optimized to fit the H_2 data (Table A-XV); this was necessary as NH_3 had been in the apparatus. A simulation was then performed, with all parameters fixed at the values just determined, on the $F + NH_3$ data (Table A-XIII).

The total rate constant used for the reaction was that given by Houston (3.94×10^{-11} cc/molec/sec)⁽⁷¹⁾. The energy-transfer rate constants for vibrational deactivation of HF(v) by ammonia were taken from those listed in ⁽⁷³⁾, for HF(v = 2-4). As these were only weakly dependent on the HF v-level being deactivated, the rate constants for deactivation of all vibrational levels were taken to be the same.

Table A-XXI
Simulator Results of Calibration Reaction

Run	SF ₆ ^a	H ₂ ^a	I.P. ^b	Distributions-- Measured (Calculated)			P _{tot} ^c
				v' = 1	v' = 2	v' = 3	
11	1.03	1.24	-1.75	.31 (.31)	.49 (.48)	.19 (.20)	.08 (.04)
12	1.41	1.41	0.0	.37 (.37)	.47 (.45)	.16 (.17)	.25 (.14)
13	1.41	1.56	0.65	.40 (.41)	.46 (.43)	.15 (.15)	.33 (.24)
14	1.58	4.76	0.65	.42 (.40)	.43 (.44)	.15 (.15)	1.00 (1.00)
15	1.66	4.91	0.0	.39 (.37)	.45 (.46)	.16 (.17)	.67 (.60)
16	1.55	5.06	-1.75	.31 (.31)	.50 (.50)	.19 (.20)	.23 (.23)
17	1.63	1.36	-1.75	.30 (.31)	.52 (.49)	.18 (.20)	.06 (.06)
18	4.26	1.44	-1.75	.27 (.28)	.52 (.52)	.21 (.20)	.22 (.14)
19	4.38	1.45	0.0	.34 (.34)	.48 (.49)	.17 (.16)	.46 (.49)
20	4.58	1.47	0.65	.38 (.38)	.46 (.47)	.15 (.15)	.64 (.94)
21	1.44	1.50	0.65	.40 (.41)	.45 (.43)	.15 (.15)	.30 (.24)

a) Flows in micromoles/sec

b) Injector distance inside Tube 2. Negative values indicate that injector was below that tube.

c) Relative total populations

The assumed initial distribution, required for the detailed rate constants, was $v' = 0: v' = 1: v' = 2 = 0.50:0.30:0.20$. This choice was made on the basis of a simple density of vibrational states calculation, for the reaction exoergicity and using the harmonic frequencies in the FNH_3 complex calculated by Goddard⁽⁷⁷⁾. The same choice of initial distribution is obtained whether all of the complex frequencies associated with the NH_2 moiety or just the near resonant ones are included in the state count. This choice also gives rise to the experimentally-observed distribution ($v' = 0: v' = 1 = 0.6:0.4$). No population of HF ($v' = 3$) by reaction [2] was allowed, as no emission was seen from that state under the conditions yielding the distribution from the primary reaction only.

Each predicted total emission intensity for the primary reaction only calculated in this way was scaled by the ratio of observed/predicted total intensity for the F/H_2 run immediately succeeding it. Thus the contribution to the observed total intensity from the primary reaction only, could be extracted.

The contribution from the secondary reaction was then calculated by the same procedure as was used to extract F/H_2 distributions in the $\text{F}/\text{H}_2/\text{NH}_3$ system, discussed in section (a), above. The vibrational distributions for $\text{F} + \text{NH}_3$, predicted by the simulator, were multiplied by the corresponding total intensities, as calculated above. The resulting values of population in each HF v-level were then subtracted from those observed experimentally (given by multiplying the observed

3

distributions by the observed total intensity). Renormalization of the resulting populations gave energy distributions from the secondary reaction.

The results are shown in Tables A-XXII and A-XXIII. The first table gives the values of the total intensities, both as observed and as predicted by the simulator for the F/H_2 and F/NH_3 simulations. The last column in the table is the predicted contribution to the experimentally-determined total intensity from the primary reaction only. The difference between that value and the observed one is the predicted contribution to the total intensity arising from the secondary reaction only.

Table A-XXIII shows the distributions from the secondary reaction, as calculated in this manner. There is a large degree of uncertainty associated with each, as is obvious from the scatter in the data. The distributions are all quite strongly peaked in $v' = 2$ of HF, however. The last entry in the table gives the average of the three calculated distributions. The errors represent one standard deviation. This result is shown in Figure A.3.10.

CONCLUSIONS

In the foregoing, experimental measurements on the F/NH_3 system were presented for which there is only one reasonable interpretation. The primary reaction,

gives rise to a cold vibrational distribution in the HF product.

Table A-XXIISimulator results of F/NH₃ total intensity.

Run (a)	Total Intensity ^(b) Observed/calculated		Derived Total Intensity for Primary Reaction ^(c)
	H ₂	NH ₃	
38	-	.062/.387	.038
39	.058/.588	-	-
40	-	.113/.830	-
41	.130/.133	-	.081
44	-	.278/1.56	-
45	.248/2.82	-	.137

a) Run numbers correspond to those in Tables A-XIII and XIV

b) Arbitrary units. The observed and calculated intensity units are not the same.

c) calculated from $\frac{P_{\text{tot}}(\text{H}_2)_{\text{exp}}}{P_{\text{tot}}(\text{H}_2)_{\text{calc}}} \times P_{\text{tot}}(\text{NH}_3)_{\text{calc}}$

Table A-XXIIIDerived HF vibrational distributions for $F+NH_2$

RUN	$P(v'=1)$	$P(v'=2)$	$P(v'=3)$	$P(v'=4)$
38	.37	.58	.05	-
40	.07	.80	.10	.03
44	.19	.67	.10	.03
ave.	$.21 \pm .15^{(a)}$	$.68 \pm .11$	$.08 \pm .03$	$.03 \pm .02$

a) one standard deviation

Figure A.3.10.

HF vibrational distribution derived for the $F+NH_2$ reaction, given in Table A-XXIII. The error bars represent one standard deviation.

This distribution is: $v' = 1 : v' = 2 = 0.6 : 0.4$. This is seen to be due to the formation of a strong hydrogen bond as the products separate. A resonance between the vibrational frequency of the HF and modes of NH_2 in this complex allows an escape of vibrational energy from the nascent HF molecule. In contrast to this, the secondary reaction,

gives rise to an inverted HF vibrational distribution. This, it is argued, is the result of a very low barrier to the direct abstraction of a hydrogen from NH_2^* . This mechanism may involve vibrationally-excited NH_2 , which is predicted to be formed in the primary step. The vibrational distribution for the product HF, when extracted from the measured distributions, is predicted to be: $v' = 1 : v' = 2 : v' = 3 : v' = 4 = 0.21 \pm 0.15 : 0.68 \pm 0.11 : 0.08 \pm 0.03 : 0.03 \pm 0.02$.

* In a very recent calculation, Goddard (77) has determined the hydrogen bond strength in the $\text{FH} \cdots \text{NH}$ system, analagous to that of $\text{FH} \cdots \text{NH}_2$, discussed above. A collinear complex is predicted, bound with respect to $\text{HF} + \text{NH}$ by 8.1 kcal/mol, using the 4-31G basis set and 5.7 kcal/mol, using the 6-311G** basis. The HF and NH bond lengths are predicted to be almost identical to their isolated values. It is thus felt that, because of the relatively small well depth (ca. 6 kcal/mol with respect to an exoergicity of 44 kcal/mol) and the very small changes

in the HF and NH₃ geometries upon formation of the hydrogen bond, the presence of this hydrogen bond will not affect the dynamics of the F + NH₂ reaction as markedly (if at all) as does the corresponding well in the exit channel of the F + NH₃ reaction.

Chapter A.4: The Reaction $O + C_2H_3 \rightarrow CO + CH_3$

A.4.1

INTRODUCTION

The reactions of ground state (3P) oxygen atoms with hydrocarbons have been the subject of considerable interest. These reactions form the basis of hydrocarbon combustion systems and are therefore of great importance. The dynamics of these reactions have been investigated by many methods. The results have been given in a recent review by Lin⁽⁵⁵⁾.

In general, the reactions of $O(^3P)$ with saturated hydrocarbons display direct dynamics - hydrogen atoms are abstracted by the oxygen, producing OH and an alkyl radical⁽⁵⁵⁾. The transition state for this process has been inferred from experimental studies⁽⁹⁶⁾ as being near collinear (C-H-O); this result has been given also by theoretical studies⁽⁹⁷⁾. In contrast to this, the reactions with unsaturated hydrocarbons are considerably more complex⁽⁵⁵⁾. They are believed to proceed via an addition of the oxygen atom to the multiple CC bond, initially forming a triplet diradical. This is then held to undergo a unimolecular fragmentation, the products of which seem to depend upon the pressure regime of the experiment.

The reaction with ethylene, in particular, has been the subject of very recent interest⁽⁹⁸⁻¹⁰⁴⁾. Early studies^(105,106) of this reaction had suggested that the products are almost exclusively HCO and CH_3 , in accordance with the Cvetanovic⁽¹⁰⁷⁾ mechanism for O-atom + unsaturated hydrocarbon reactions. Quite recently, however, it has been reported that under single collision conditions the primary (and possibly the exclusive) products are $C_2H_3O + H$ ^(98,99,102). Under higher pressure conditions (80-760 Torr), both sets of products were observed by

Hunziker⁽¹⁰⁰⁾. The interpretation of these findings was aided by ab-initio calculations of Dupuis, Lester and coworkers⁽¹⁰¹⁾ on the O/C_2H_4 system. It was postulated in reference⁽¹⁰⁰⁾ that in the absence of collisions, the only reactive pathway open to the initially-formed triplet diradical was to eliminate a hydrogen atom, forming the vinoxy (C_2H_3O) radical. Under higher pressure conditions, the triplet could be collisionally transformed into an isoenergetic singlet state, which could then give rise to the $HCO + CH_3$ products. This interpretation has been questioned, however. In a very recent study, no pressure dependence of the total rate constant of the O/C_2H_4 reaction was found in the pressure range 0.5-5 Torr⁽¹⁰⁴⁾.

The spectroscopy of the vinoxy radical has been studied in the gas phase^(100,108) and in an Ar matrix⁽¹⁰⁹⁾. The latter work is of particular interest to this study. Jacox⁽¹⁰⁹⁾ observed the products of co-deposition of F-atoms and acetaldehyde (C_2H_5CHO) in an Ar matrix using infrared absorption. She found that after ultraviolet irradiation the spectrum assigned to the CH_2CHO product vanished and strong absorptions appeared in the CO and CH_3 regions. The lowest photon energy at which this photodissociation was found to occur was about 95-kcal/mol.

In two previous papers from this laboratory^(11,110), the observation of highly vibrational excited CO in the reaction system $O/F/C_2H_4$ was reported. This excited CO was attributed to the reaction of O-atoms with vinyl radicals, formed in the F/C_2H_4 reaction. In this case, a vinoxy radical can be formed reactively, with ca. 120 kcal/mol of excess energy. In the following chapter, these results are discussed in detail.

A.4.2.

EXPERIMENTAL

For all experiments to be discussed below, the reagent inlet configuration B of the previous chapters was used. Vinyl radicals were generated by the reaction of F-atoms with ethylene (ethene). This reaction proceeds via two channels^(111,112): one (75%) produces vinyl fluoride and an H-atom and the other (25%) yields HF and acetylene. SF_6 (Matheson) was used at all times (in tube 2) as the F-atom precursor. Ethylene (Matheson CP 99.5%) was introduced in one of two ways: either it was metered directly into the injector, or it was metered into the injector after passing through a molecular sieve (Linde 5A) trap kept at -80°C by a dry ice/methanol slush bath. No difference in the results was observed between the two methods of introduction.

Oxygen atoms were produced in a microwave discharge of molecular oxygen (Matheson and Air Products, both ED grade, 99.6%) flowing in tube 1. The O_2 was used directly, without further purification.

For these experiments it was necessary to use high reagent flows and to increase the pressure in the reaction zone by partially closing the gate valve through which the reaction vessel was evacuated. Under these conditions, the total pressure in the vessel never exceeded 5×10^{-4} Torr, as measured by a cold cathode ionization gauge situated behind the vertical cooled vanes.

The preliminary experiments in the $\text{O/F/C}_2\text{H}_4$ system were done using the InSb detector. Because the sensitivity of this detector decreases rapidly for frequencies less than ca. 1900 cm^{-1} , the later

experiments were done using a HgCdTe detector (Santa Barbara Research Corp.), which is sensitive to about 1600 cm^{-1} .

A.4.3

RESULTS AND DISCUSSION

(a) Experimental Results

The reaction used to generate the vinyl radicals:

has an exoergicity (at 0K) of 29 kcal/mol. This is sufficient to populate only ($v' = 1,2$) of HF; if reagent translational and rotational energy are included HF($v' = 3$) becomes just accessible. As reported previously⁽⁸⁾, under conditions of high F-atom concentration, emission is observed from vibrationally-excited HF in v -levels up to and including $v' = 9$. As these levels are thermochemically inaccessible to the primary reaction, their presence is attributed to the reaction of F-atoms with vinyl radicals:

This reaction has an exoergicity at 0K of 98 kcal/mol and can therefore populate HF($v' \leq 10$). The measured HF vibrational populations in the latter reaction decrease monotonically with v -level, until the signal disappears into the noise. This vibrational distribution was well fitted^(8b) by a statistical calculation for the elimination of HF from vinyl fluoride (this result was discussed briefly in a previous chapter).

In the present work, under conditions of high reagent flows (SF_6 :7, O_2 :41, C_2H_4 : 10; all in $\mu\text{mol/s}$), the injector raised to just inside tube 2 (which ended 1.4 cm inside tube 1) and the gate valve partially closed (measured vessel pressure = 4×10^{-4} Torr), this high- ν HF emission is seen as well. A portion of the HF spectrum thus obtained, using the InSb detector at a resolution of 0.24 cm^{-1} , is shown in Figure A.4.1. The P-branch transitions of $\text{HF}(v'=6-9)$ are indicated. It can be seen that the emission intensity (and thus population) drops monotonically with ν -level until it sinks into the noise. The only source of the high- ν HF emission is the $\text{F/C}_2\text{H}_3$ reaction. This result serves to indicate that vinyl radicals are present in the system.

Emission from vibrationally excited CO is observed under the same conditions as those which yield the emission from high ν -levels of HF. The upper trace of Figure A.4.2 shows the CO region of the same spectrum as is shown in the previous figure. The lower trace of Figure A.4.2 shows the result obtained when the discharge in tube 2 is turned off while the SF_6 is kept flowing. It is plotted with the same vertical gain as the upper trace. Also shown are the band origins and P- and R-branch ranges for CO vibrational levels 1-7.

Inspection of Figure A.4.2 reveals several interesting features. First, when both O-atoms (flowing in tube 1) and F-atoms (in tube 2) are present, substantial vibrational excitation is observed in the CO product (upper trace). This excitation extends to beyond the limit of sensitivity of the InSb detector (ca. 1900 cm^{-1}). The lower trace shows that when there are no F-atoms present in the system, and therefore no vinyl radicals, there is still emission observed from vibrationally

Figure A.4.1.

A portion of the HF emission spectrum observed from the $O/F/C_2H_4$ system. The P-branch transitions for v -levels 6-9 are indicated. HF v -levels higher than $v'=3$ are populated only by the $F+C_2H_3$ reaction.

Figure A.4.2.

The CO emission spectrum recorded under the same conditions as those of the previous figure, using the InSb detector. The upper trace shows the spectrum recorded when F-atoms are present; the lower shows that observed when F-atoms (and hence, vinyl radicals) are absent. The band origins and P- and R-branch ranges for $v=1-7$ are indicated. The loss of sensitivity of this detector at frequencies less than about 1950 cm^{-1} is clear.

excited $\text{CO}(v' = 1,2)$. The origin of this emission must lie in the $\text{O}/\text{C}_2\text{H}_4$ system, as these are the only reactive species present. This point will be addressed in more detail below.

In order to improve upon the signal-to-noise ratio in the CO region and to more completely resolve the individual ro-vibrational lines of CO, an experiment was carried out using the HgCdTe detector and a resolution of 0.06 cm^{-1} . The reagent flows were higher than those used to produce the results shown in figures A.4.1 and A.4.2; they were: SF_6 : $32 \text{ } \mu\text{mol/s}$, O_2 : $220 \text{ } \mu\text{mol/s}$, C_2H_4 : $56 \text{ } \mu\text{mol/s}$. As before the gate valve was partially closed for this experiment. However, the measured vessel pressure did not exceed $2 \times 10^{-4} \text{ Torr}$.

For this experiment the injector was withdrawn 1.5 cm inside tube 2 (which terminated 2.7 cm inside tube 1). This had the effect of causing substantial vibrational deactivation in the HF which had previously been observed to emit from v-levels up to $v' = 9$. Under these conditions, no emission was seen from $\text{HF}(v' > 3)$; the populations in $v' = 1-3$ exhibited a strongly-decreasing trend as a function of v-level. Figure A.4.3 shows the same region of the HF spectrum as was illustrated in Figure A.4.1. The effect on the HF vibrational populations of raising the injector to such an extent is clearly shown. (It should be noted here that the HgCdTe detector is not as sensitive in this region as is the InSb detector. This fact is not sufficient to explain the total absence of observed emission from v-levels > 3 , however.)

The CO spectrum, recorded at 0.06 cm^{-1} resolution under the same conditions as those pertaining to Figure A.4.3, is illustrated

Figure A.4.3.

A portion of the HF spectral region, recorded under high reagent flow, high injector location conditions in the O/F/C₂H₄ system. The HgCdTe detector was used in this experiment. No emission is seen from HF($v>3$) under these conditions.

Figure A.4.4.

The CO spectrum recorded under the conditions of the previous figure. The spectral resolution is 0.06 cm^{-1} in this plot; the HgCdTe detector was used. Again, the upper trace shows the result obtained when F-atoms are present; the lower, that obtained with no F-atoms. The band origins and ranges for $v=1-10$ are indicated.

in Figure A.4.4. Again, the upper trace represents the result obtained when both discharges (SF_6 and O_2) are on and the lower trace shows the spectrum obtained when the SF_6 discharge is switched off. The upper trace this time shows measurable emission from all CO v-levels ($v' \leq 14$). This result demonstrates clearly the improved sensitivity of the HgCdTe detector over the InSb one at frequencies less than ca 1900 cm^{-1} . For clarity, only the first ten ($v' = 1-10$) band origins and ranges are illustrated.

The lower trace, taken under otherwise identical experimental conditions to that displayed above it, shows the emission observed when the SF_6 microwave discharge is off. Again, emission is observed from vibrationally excited CO; in this case $\text{CO}(v' \leq 3)$ is seen. No emission from vibrationally excited CO is observed when the O_2 discharge is off.

The vibrational populations derived from the spectra shown in Figure A.4.4 are displayed in Table A-XXIV and Figure A.4.5. (The vibrational distributions have been normalized such that $\sum_{v'} P_{v'} = 1.0$). A substantial contribution to the first three observed v-levels from the $\text{O}/\text{C}_2\text{H}_4$ system is apparent in the $\text{O}/\text{F}/\text{C}_2\text{H}_4$ case. A direct subtraction of this contribution to each v-level is not warranted, however, as the concentration of ethylene is not the same in the two systems. (When F-atoms are present, the C_2H_4 concentration is decreased by an unknown amount via reaction.) For this reason, the discussion of the $\text{O}/\text{F}/\text{C}_2\text{H}_4$ system which follows will restrict itself to the CO levels ($v' \geq 4$). The renormalized populations (excluding $v' = 1-3$)

Table A-XXIVCO vibrational distributions observed in the O/F/C₂H₄ and O/C₂H₄ systems

	Experiment	
	O/F/C ₂ H ₄	O/SF ₆ /C ₂ H ₄
CO(v'=1)	.255	.714
2	.120	.210
3	.082	.077
4	.066 (.122)	(P _{tot} =0.18)
5	.061 (.113)	
6	.058 (.107)	
7	.054 (.099)	
8	.051 (.093)	
9	.047 (.087)	
10	.045 (.083)	
11	.039 (.072)	
12	.039 (.072)	
13	.029 (.054)	
	(P _{tot} =1.0)	

Figure A.4.5.

CO vibrational populations derived from the spectra shown in Figure A.4.4. The upper distribution corresponds to the upper trace in that figure; the lower, to the lower trace. A strong contribution to the first three v-levels of CO from the O/C_2H_4 system is apparent.

are given in brackets in the Table and are plotted in Figure A.4.6.

Based on the results of the F/HCO system, viz, that the measured CO vibrational distribution is much less sensitive to the experimental conditions than is that of HF, the distributions given in the Table and Figures are believed to be free of substantial vibrational deactivation effects. They thus represent a lower limit to the amount of vibrational excitation in the nascent CO molecule.

(b) Emission from O/F/C₂H₄

The strong CO emission shown in the upper traces of Figures A.4.2 and A.4.4 is observed only when both F- and O-atoms are present in the system, as well as C₂H₄. It must therefore be the result of a secondary process involving O-atoms and the products of the F/C₂H₄ reaction.

Reaction [1] is reported^(111,112) to yield two sets of products:

The only secondary process in this system which is energetic enough to produce the observed high vibrational levels of CO is the reaction:

Other energetically-viable routes which require the presence of both F- and O-atoms are the multi-step sequences:

Figure A.4.6.

The renormalized CO vibrational distribution, for the $\text{O/F/C}_2\text{H}_4$ system, showing the distribution in $v'=4-10$.

and:

Only the last reactions in each sequence are exoergic enough to populate $CO(v' = 14)$. Thus, if either or both of these are responsible for the highly vibrationally excited CO observed in the system, a four-step mechanism is required. This is highly unlikely in the current apparatus; the concentrations of product species are orders of magnitude lower than those of reactants. Thus, even if gas-kinetic cross sections are assumed for all atom/radical reactions in the system, the density of CO formed in the last reaction step would be too small for its observation in the present apparatus.

The emission observed in the $O/F/C_2H_4$ system is therefore attributed to the reaction:

The very gradually-decreasing vibrational distribution, shown in Figure A.4.6, is clearly much more highly excited than that arising in the

F/HCO system, discussed in a previous chapter. It will be shown below that this distribution is also more excited than that predicted on statistical grounds for the decomposition of a C_2H_3O complex. This result is quite surprising, given the fact that the vinyl radical must undergo a substantial rearrangement (involving an H-atom migration) in order that the reaction (yielding the observed CO product) proceed.

The intermediate complex (C_2H_3O) expected to be formed in this reaction has been the subject of some recent theoretical⁽¹¹³⁾ and experimental^(100,108,109,114) studies. The vinoxy radical (CH_2CHO) is a bound species. Three low-lying electronic states have been characterized both spectroscopically^(100,108) and by ab-initio calculations⁽¹¹³⁾. The ground state ($^2A'$ in C_s) has predominantly the "formyl-methyl" isomeric structure, illustrated in Figure A.4.7, as opposed to the "vinyloxy" structure (also $^2A'$ in C_s). In the former, the CO bond order is close to two and the CC bond order close to one. The latter isomer has these bond orders reversed. The energetic splitting between the states arising from these two electronic structures has been experimentally determined to be about 83 kcal/mol^(100,108). Both arise⁽¹¹³⁾ from electronic structures in which the unpaired electron is in a pi-orbital and the lone pair associated with the O-atom is in the plane of the radical. These are illustrated in Figure A.4.7.

Another low-lying state is predicted⁽¹¹³⁾ to arise from the case where the unpaired electron is centered on the oxygen, but is

Figure A.4.7.

Schematic representations of the three lowest states of the C_2H_3O radical
(113).

in the plane of the radical ($^2A'$). This state has also been observed experimentally⁽¹⁰⁰⁾; it lies 23 kcal/mol above the ground state. It is shown schematically in Figure A.4.7, as well.

All three of these states correlate directly (in C_s symmetry) to ground state reactants. If C_s symmetry is retained throughout the reactive encounter, the $^2A'$ state is the only one which will correlate directly to ground state products. This state also correlates to the ground state of H_3CCO (acetyl radical), i.e. a 1,2 hydrogen atom migration is allowed to take place from the $^2A'$ state. This migration, followed by CC bond cleavage, is the mechanism intuitively expected to produce the observed CO product. A schematic correlation diagram (in C_s symmetry) incorporating these points and the energetics^(100,108,113) is displayed in Figure A.4.8.

Although these correlations clearly permit the suggested reaction to occur, the complexity of this system calls into question the validity of such correlation diagrams. It seems extremely unlikely that the system will retain even C_s symmetry throughout the reaction. In this event all states of the vinoxy intermediate are likely to give rise to H-atom migration and the subsequent decomposition to CO and CH_3 .

Statistical calculations analogous to those described in a previous chapter were carried out for this system. These assume that the measured CO vibrational distribution is the result of the unimolecular decomposition of a long-lived C_2H_3O complex. For the calculations, the vibrational frequencies corresponding to isolated CH_3 ⁽¹¹⁵⁻¹¹⁷⁾ were used. These are quite similar to those frequencies of acetaldehyde which are

Figure A.4.8.

Schematic correlation diagram for the $O+C_2H_3 \rightarrow CO+CH_3$ reaction.

primarily methyl in character, given by Herzberg⁽⁴³⁾. It is thus expected that the density of accessible CH_3 states is adequately represented in the calculation. The values used for the vibrational frequencies, their symmetry types (in D_{3h}) and the assumed anharmonicities are given in Table A-XXV.

Two reasonable vibrational frequencies were chosen for the nascent CO: 1800 cm^{-1} , which corresponds to the CO stretching frequency in CH_3CO ⁽¹⁰⁹⁾ and 1500 cm^{-1} , corresponding to that of the vinoxy radical⁽¹⁰⁸⁾. One might expect that the vibrational frequency of the CO fragment in the region of the potential energy surface where the energy partitioning occurs would lie fairly close to these values. Unlike the case of FHCO , discussed previously, these frequencies are considerably smaller than that of the free CO molecule.

The results, plotted in Figure A.4.9, show that the calculated statistical distribution does not match the observed one. The points in the figure represent the measured distribution; the two solid lines show the results for $\omega(\text{CO}) = 1800\text{ cm}^{-1}$ (coldest distribution) and $\omega(\text{CO}) = 1500\text{ cm}^{-1}$. Neither of these predictions comes close to matching the observed data; the latter is much more highly excited.

If it is accepted that the reaction proceeds via formation of a complex followed by its unimolecular decay, this result implies that the density of states accessible to the CO is greater than that used in the calculation. The vibrational frequency appropriate to the CO moiety in the region of free energy flow may be smaller than the ones used herein. This, by itself, does not appear to be a likely

Table A-XXV

Frequencies, anharmonicities, etc. used in STAT calculation

ν	freq./cm ⁻¹	anharmonicity (cm ⁻¹)	irreducible representation (D _{3h} point group)
1	3044	30	a ₂ '
2	617	10	a ₂ "
3	3162	30	e'
4	1396	20	e'

Figure A.4.9.

The measured vibrational distribution (squares) and statistical predictions for the CO product of the $\text{O} + \text{C}_2\text{H}_3$ reaction. Two different CO vibrational frequencies were used in the density of states calculation; the more-excited prediction corresponds to a frequency of 1500 cm^{-1} for that molecule, the less excited to a frequency of 1800 cm^{-1} . Clearly, the predictions are considerably less excited than the observed distribution.

cause for the large difference between the predicted and observed distributions. Only a slight difference in the statistical predictions is seen upon decreasing the CO vibrational frequency from 1800 to 1500 cm^{-1} . This is because, with six (as opposed to one) vibrational modes, the CH_3 fragment dominates in the density of states calculation. However, if some of these modes are not excited in the reaction, the fraction of the phase space occupied by the CO vibration will increase. This will result in the prediction of a more excited distribution by the calculation.

There are no modes in the CH_3 fragment which, a priori, are not expected to be excited in the reaction. The hydrogen migration is expected to cause excitation in the various C-H stretching and bending modes; the change in structure from pyramidal (in H_3CCO) to planar (in CH_3) is expected to excite the "umbrella" out-of-plane bending mode. No theoretical calculations of the reaction coordinate for the decomposition of $\text{C}_2\text{H}_3\text{O}$ are available. Without any additional information on the system, a further decrease in the CO vibrational frequency used in the calculation seems unwarranted.

It is thus concluded that the CO product of the $\text{O}/\text{C}_2\text{H}_3$ reaction is formed with more vibrational excitation than is expected from a purely statistical partitioning of the reaction energy. The rotational distributions, shown in Figure A.4.10 for v-levels 4-10, are quite broad. They extend to very high rotational states for all v-levels observed in this experiment. Since both vibration and rotation of the CO thus appear to be highly excited, it is clear that a less-than-statistical

Figure A.4.10.

The CO rotational distributions for v -levels 4-10 from the $O+C_2H_3$ reaction, derived from the upper trace of Figure A.4.4.

amount of the reaction energy is partitioned into the CH_3 product ro-vibrational states and/or relative translation of the two fragments.

The reason for the greater-than-statistical amount of energy partitioned into CO vibration likely lies in the fact that the CO bond is being formed in the reaction. If the potential energy surface for the reaction is attractive ⁽⁶²⁾ (as is expected for this atom/radical system possessing a deep potential well), then a large percentage of the reaction energy is released as the O-atom approaches the radical. If the barrier to hydrogen atom migration in the vinoxy radical is not too high, the latter process may take place before the (bound) system has lived long enough to randomize the energy which is initially deposited in the C-O bond. This would lead to a greater-than-statistical fraction of the exoergicity appearing in CO vibration, as is observed experimentally.

(c) Emission from $\text{O}/\text{C}_2\text{H}_4$

In the preliminary work on the $\text{O}/\text{F}/\text{C}_2\text{H}_4$ system, reported in (11,110), vibrational emission from $\text{CO}(v' = 1,2)$ was observed when no F-atoms were present (see Figures A.4.2, A.4.4. This was postulated as being formed in the $\text{O}/\text{C}_2\text{H}_4$ reaction ^(11,110). This process:

has a total energy available to products of 14-16 kcal/mol ⁽¹¹⁾ - enough to populate up to $v' = 2$ of CO only. The present results, in which $\text{CO}(v' = 3)$ was observed, indicate that this emission must arise from some other source.

Two possibilities exist, involving secondary reactions of the O/C_2H_4 system, to explain the CO vibrational excitation. Hunziker et al.⁽¹⁰⁰⁾ measured a branching ratio of 0.35 ± 0.09 for production of HCO in the O/C_2H_4 reaction. This product is attributed to the "pressure-dependent fragmentation"⁽¹⁰⁷⁾ of the C_2H_4O radical initially formed in the reaction. This process is believed to occur⁽¹⁰⁰⁾ via a collisionally-induced spin flip of the triplet diradical to an isoenergetic singlet state. This state is expected⁽¹¹⁸⁾ to have a low barrier to the 1,2 H-atom migration, and subsequent decomposition to $HCO + CH_3$.

Hunziker et al.⁽¹⁰⁰⁾ found no pressure dependence of the product branching ratios between ca. 80 and 760 Torr. Furthermore Peeters,⁽¹⁰⁴⁾ in a very recent report, found no falloff in the O/C_2H_4 rate constant at pressures down to as low as 0.5 Torr. The latter data imply that the cross section for any collisionally-induced spin change ultimately producing HCO must be extraordinarily large. However, if HCO is somehow formed in the O/C_2H_4 reaction, then it could react with excess O-atoms in the system to produce CO and OH.

As mentioned in a previous chapter, this reaction has been^(44,54) reported to give rise to substantial vibrational excitation in the OH product. As was reported there, no OH emission was observed by the present author in the $O/F/H_2CO$ system. None was observed in the O/C_2H_4 system either. Although the reaction could proceed without producing vibrationally excited OH, this seems highly unlikely; the most exoergic channel:

is probably the dominant one.

The other possible source of the CO observed in the O/C₂H₄ system is the reaction of O-atoms with the vinoxy radicals formed in the primary step:

By analogy to the F/HCO system, this reaction, though quite exoergic, would not be expected to yield high vibrational excitation in the CO product. This is because the ~~C-O~~ bond is not formed in the reaction; any excitation in it must arise from energy flow between nascent products of the reaction. The measured vibrational distribution is a strongly decreasing, though non-Boltzmann, function of v-level as was observed also in F/HCO.

No further experiments were undertaken on this system. As discussed above, the possibility of observing vibrational emission from the products of tertiary (or higher order) reactions in the current apparatus is very small. The only secondary reactions which could conceivably give rise to the observed emission are the two discussed above. (The reaction:

is also exoergic enough to populate $v' = 3$ of CO. However, the branching ratio for formation of ketene in the O/C₂H₄ reaction is

reported as $< 5\%$ ⁽⁵⁵⁾; the formation of this product also involves collisional stabilization of the radical initially formed in reaction [6]⁽¹¹⁸⁾. For these reasons, it is considered highly unlikely that this is the origin of the excited CO.) For the reasons mentioned above, it is not likely that the reaction of O-atoms with formyl radicals is responsible for the observed CO emission. The origin must therefore lie in the reaction with vinoxy radicals which are formed in the primary step.

CONCLUSIONS

The reaction of O-atoms with vinyl radicals has been shown to produce vibrationally excited CO. This product is formed with considerably more vibrational excitation than is expected from the unimolecular decomposition of the vinoxy radical, if it is assumed that all accessible product states are equiprobable. This implies either that the vinoxy complex does not live for a long enough time to completely randomize the available chemical energy, or that there is a "bottleneck" in the phase space of the excited vinoxy which prevents the free flow of energy out of the nascent C-O bond and into the CH_3 fragment. The high degree of CO vibrational excitation observed thus results from the fact that the energy, initially deposited into the CO bond as the vinoxy complex is forming, does not completely escape before product separation. The CO thus formed possesses more vibrational energy than would be the case for a completely statistical outcome.

Vibrationally excited CO is also observed in the O/C₂H₄ system in the absence of vinyl radicals. This is postulated as arising from the secondary reaction of O-atoms with vinoxy radicals,

which are formed in the O/C₂H₄ primary reaction. The strongly decreasing measured vibrational distribution is consistent with this assignment. Based on the results given previously for the F/HCO system, a large amount of energy is not expected to be deposited into the already-existing CO bond, unless the lifetime of the intermediate complex is very long.

Summary of Experimental Results

SUMMARY OF EXPERIMENTAL RESULTS

In the preceeding chapters, the energy disposal measured in three atom/radical reactions was examined. It was demonstrated in those chapters that the observed product energy distributions are quite different in the three cases, in spite of the common existence of potential energy wells accessible to reactants. As indicated previously, the presence of a well in a reactive PES often gives rise to a statistical distribution of reaction energy among the products.

In Chapter A.2, the energy disposal in both products of the $F + HCO \rightarrow HF + CO$ reaction was discussed. The reaction is highly exoergic and, if it proceeds in C_s symmetry, must take place on a PES which correlates to the strongly bound FHC0 molecule. The monotonically decreasing vibrational distributions observed for each product (ie, $HF(v' \leq 5)$, $CO(v' \leq 5)$) imply that the reaction does, indeed, proceed via the decomposition of an FHC0 complex. Although the weakness of the H-CO bond^(44,45) and the fact that the system is not constrained to maintain C_s symmetry suggest a direct abstractive route to products is also possible, no evidence for this was obtained in the present work. If this route was important, one would expect substantially more excitation in the product HF vibration and little or no excitation in the product CO, as is observed in several other systems of the type: $A + BCD \rightarrow AB + CD$ ^(2,119,120)

The present results suggest that the dominant feature on the reactive surface is the deep well corresponding to FHC0. In this

respect, they are similar to the results of recent trajectory studies of the $O(^1D) + H_2$ reaction. In studies carried out on two different PES's^(137,175), it was found that the vast majority of reactive trajectories passed through the well corresponding to ground state H_2O ^(121,178), in spite of very small or non-existent barriers to the direct abstraction on these surfaces.

The HF vibrational and rotational distributions obtained in the present work were seen to be statistical, with the partitioning of reaction energy occurring in the exit channel. The CO distributions were considerably less excited than would be expected of a completely statistical partitioning of the available energy among all accessible product modes. This is due to the much smaller changes in the CO properties (bond length, vibrational frequency), with respect to those of HF, over the course of the reaction. In this regard, the results approach those of several other $A + BCD$ type systems^(2,119,120), as mentioned above.

In Chapter A.3, the $F + NH_2$ reaction was demonstrated to yield a strongly inverted vibrational distribution in the HF product. In this respect, it is similar to many other $F + H-R$ reactions, in which a substantial amount of the reaction energy is deposited into vibration in the product $HF^{(4)}$. The present result was seen to be due to a very small barrier to the direct abstraction mechanism for the reaction, on the $^3A'$ surface. It thus differs from the isoelectronic $F + OH$ system, in which the reaction is forced to take place via the formation of a (bound) FOH complex because of the height of the barrier to the

direct reaction⁽¹⁰⁾. As the former mechanism involves a surface switch, from a singlet to a triplet PES, it is considerably less probable than any other mechanism which leads directly to products. In the present case, the direct reaction on the $^3A''$ surface is accessible to the reactants, because of the low barrier height on that surface. Although a surface switching mechanism, analagous to that of F/OH, cannot be eliminated on the basis of the present work, the predominance of the direct mechanism is clearly indicated by the observed HF vibrational distribution.

The reaction of O-atoms with vinyl radicals was discussed in Chapter A.4. In this case, the CO product is formed with considerably more vibrational excitation than is predicted for a completely statistical partitioning of reaction energy. Based on the observed cutoff in the CO emission, the second product of the reaction must be CH_3 . The reaction mechanism must therefore involve an H-atom migration and subsequent-CC bond cleavage - considerably more complex than those postulated for the other reactions discussed herein. In view of this, it seems somewhat surprising that the CO vibrational distribution is not statistical. However, it is the CO bond which is formed in the reaction; it is into this nascent bond that the exoergicity is initially deposited. The conclusion is therefore that the C_2H_3O complex does not live long enough to distribute this energy statistically among all accessible product modes. A less-than-statistical amount of this energy is thus predicted to be partitioned into the internal modes of the CH_3 product and/or relative translation of the two products.

C

In all three of the reactions studied in this work, the newly-formed bond is predicted to carry away from the reaction more energy than the previously existing bond(s). This is clearly seen in the F/NH_2 reaction, in which the resulting HF vibrational inversion is observed to be very strong. In the two reactions proceeding via a bound intermediate (F/HCO and O/C_2H_3), this effect is also observed, but not as strongly as in the F/NH_2 system. In these cases, the effect is due to an incomplete randomization of reaction energy over the modes of the intermediate complex formed in the reaction. A less-than-statistical amount of this energy is partitioned into the previously existing bond(s) in each case.

SECTION B: Ab-Initio Study of Surface Crossings

in the $O(^3P, ^1D) + H_2 \rightarrow OH + H$ System

Chapter B.1: General Introduction to Section B

B.1.1

INTRODUCTION

In the Experimental Section of this work, the dynamics of several atom/radical reactions were discussed. These systems shared a common feature - the presence of wells in potential energy surfaces accessible to the reagents. The presence of these wells was seen, in some instances, to influence the dynamics of the reaction a great deal. The interpretation of the experimental results relied, to varying extents, on the knowledge of features of the reactive potential energy surface(s), as given by ab-initio calculations.

In the Theoretical Section of this work which follows, ab-initio calculations of another system exhibiting a potential minimum are described. In the O/H₂ system, there is a deep potential well corresponding to ground state H₂O. This correlates to the first excited state of the oxygen atom - O(¹D). The lower energy O(³P)/H₂ potential energy surface(s) are uniformly repulsive, but lead to the same products - OH(²Π) + H(²S) as does the lowest energy singlet surface. There is thus a crossing of the singlet and triplet hypersurfaces as the oxygen atom approaches the H₂.

This crossing was of interest for a number of reasons which are discussed more fully below. In brief, it was felt that a mechanism involving a switch from triplet to singlet hypersurfaces might explain the observed low temperature kinetics of the ground state reaction:

The possibility of such a surface switching mechanism had been demonstrated in the F/OH system⁽¹⁰⁾, in which the analagous surface crossing takes place in the exit channel.

Ab-initio calculations were therefore carried out on both the singlet and triplet hypersurfaces of the O/H₂ system, with the object of determining whether the surface crossing mechanism was energetically feasible. In this chapter, the methods used to calculate the surfaces are described in general; the following chapter reports the results and their interpretation.

(a) Potential Energy Surfaces

Quantum mechanically, the stationary states of a system of interacting nuclei and electrons are given by the solutions of the Schrodinger equation for the system:

$$\hat{H}\psi_n = E_n\psi_n \quad [1]$$

- where $\hat{H}$ is the Hamiltonian operator, ψ_n , the set of allowed wave-functions and E_n the corresponding state energies, n being the quantum number. The Hamiltonian is composed of kinetic and potential energy terms for all particles (nuclei and electrons) in the system. It contains terms in both nuclear and electronic coordinates and is given by:

$$H = -\sum_A \frac{\hbar^2}{2m_A} \nabla_A^2 + \sum_{A \neq B} \frac{Z_A Z_B}{r_{AB}} e^2 - \sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_A \sum_i \frac{Z_A e^2}{r_{A,i}} + \sum_i \sum_{i \neq j} \frac{e^2}{r_{ij}}$$

In this expression, nuclear coordinates are denoted by capitals; lower case letters indicate electron coordinates. The terms in (2) refer

respectively, to nuclear kinetic energy, nuclear-nuclear repulsion, electron kinetic energy, electron-nuclear attraction and electron-electron repulsion.

It is often assumed (Born-Oppenheimer approximation) that because the electron mass is many orders of magnitude smaller than nuclear masses, the electrons respond instantaneously (on the time scale of nuclear motion) to any change in the nuclear coordinates. If this approximation holds, the nuclear motion can be considered as a separate problem and terms in nuclear coordinates only separated out of the Hamiltonian. This results in the electronic Schrodinger equation:

$$H^{el} \psi_n^{el} = E_n^{el} \psi_n^{el} \quad [3]$$

in which the nuclear coordinates are present as parameters only.

In a practical sense, this means that the nuclear coordinates can be considered to be fixed while the electronic Schrodinger equation is solved. The latter is then solved (in principle) for all possible nuclear coordinates of the system. The result is a tabulation of system energies as a function of nuclear positions - a potential energy hypersurface. (Because of the multidimensional nature of the problem, the term "hypersurface" is used to describe the energy as a function of nuclear positions. This term is somewhat cumbersome, however, and in what follows the term "surface" is often used in its place, where such usage does not lead to confusion.)

The ideal method of calculating these potential energy surfaces (PES's) is to solve exactly the Schrodinger equation for all possible

nuclear coordinates. This approach presents almost insuperable difficulties for all but the smallest systems, however. To describe the surface accurately, a large number of points (corresponding to different nuclear position) must be calculated. This is a difficult and expensive task in itself; it is made more so by the stipulation that all regions of the surface be described equally well. In addition to this already formidable task, there must be some prescription for the choosing of points on the surface to calculate, and to interpolate smoothly between them.

The difficulties associated with strictly ab-initio methods of calculating PES's make alternate approaches quite attractive. These can take two basic forms. In the first, the calculation relies entirely upon empirically determined input data to generate the PES. A functional form for the description of the surface is chosen and this is fitted to what experimental information there is available on the system in question. An example of this type of calculation, relevant to the O/H_2 system, is the surface for ground state H_2O , derived by Sorbie and Murrell⁽¹²²⁾. This consisted of three diatomic terms, describing the three possible diatomic fragments, and a three-body interaction term. The former terms were given by the known spectroscopy of the two molecules HH and OH . The interaction term was a polynomial in the three interatomic distances, with coefficients determined by a least squares fit to experimentally determined force constants for the H_2O normal modes. This polynomial included "damping" terms, which adjusted the range of the three-body interaction.

The surface thus derived gave a very good representation of the region close to the equilibrium geometry of H_2O ⁽¹²²⁾. This is to be expected, as it is this region which was fitted to experimental data. However, the surface predicted a potential minimum for the collinear approach of oxygen to H_2 and also failed to predict a barrier to the spatially forbidden dissociation of linear H-O-H : $\text{HOH } ^1\Sigma^+ \rightarrow \text{OH}(^2\Pi) + \text{H}(^2\text{S})$. These features of the Sorbié-Murrell surface serve to illustrate the limitations of totally empirical PES's. In regions of the surface for which no experimental data is known, the actual form of the energy expression gains a high degree of importance. There is no a-priori way of determining whether features of the surface in these regions are genuinely predicted, or are merely artifacts of the analytical potential energy expression used. The same argument holds for any method which relies on large-scale interpolations between "known" regions of hyperspace. In the construction of PES's for chemical reactions, these methods are not rigorous and can give rise to misleading results.

Another approach which is often taken in the construction of PES's is to cast the Hamiltonian in such a way that an analytical expression for the energy as a function of nuclear positions is the result. Approximations and empirical data are then introduced, so as to make the solution more tractable. These methods are thus labelled "semiempirical". They are to be distinguished from semiempirical methods of calculating single points on a PES, such as CNDQ, INDO, etc.

The most commonly used of these semiempirical methods are the LEPS (for London, Eyring, Polanyi and Sato) ^(123,124) method and its

extensions⁽¹²⁵⁾, and the DIM (for Diatomics in Molecules) method⁽¹²⁶⁾ and its extensions^(127,128). The former method is treated in some detail by Eyring and Lin⁽¹²⁹⁾; the latter by Tully⁽¹³⁰⁾. A very brief description of each is given below.

The LEPS method is fundamentally based on the London⁽¹³¹⁾ treatment of H_3 . As such, it is only rigorously correct for a system of three interacting 2S atoms. In its extended form⁽¹²⁵⁾, it is written in terms of two-body coulomb (Q) and exchange (J) integrals:

$$V(r_1, r_2, r_3) = Q_1 + Q_2 + Q_3 - (J_1^2 + J_2^2 + J_3^2 - J_1 J_2 - J_1 J_3 - J_2 J_3)^{1/2} \quad [4]$$

In this expression, the Q_i and J_i are functions of Morse and "anti-Morse" energy parameters, modified by a "Sato parameter"⁽¹²⁴⁾

The latter bears a formal resemblance to the quantum mechanical overlap integral, but is generally used as an adjustable parameter.

The Morse parameters required to calculate the Q_i and J_i can be those determined experimentally, or can also be used as adjustable parameters.

Because of their simple analytical nature, LEPS surfaces have enjoyed a wide popularity in dynamics studies. For some systems, they have reproduced experimental results quite well.^(132,133)

In general, however, they suffer from a lack of flexibility^(133a)

As explained by Laidler⁽¹³⁴⁾, the lowest energy approach of atom A to molecule BC is always predicted to be the collinear one. This is, of course, not always the case (i.e., in the present example of $O(^1D) + H_2$). Another problem inherent in the LEPS method is that adjustment of one region of the surface results in changes in other regions as

well⁽¹³⁵⁾, which may not be at all desirable. In spite of these general problems, in systems to which the method is suited, it provides a simple and reasonable potential energy surface. (Schatz⁽¹³⁶⁾, in a review of published $O(^3P)/H_2$ surfaces, cited the LEPS surface of⁽¹³³⁾ as one of the best.)

The method of Diatomics in Molecules^(126,130) describes the energy of a molecule in terms of electronic state energies of its constituent atomic and diatomic fragments. In the case of three 2S atoms, it reduces to the LEPS method. The state energies of the fragment species can be experimentally determined or, for states inaccessible to experiment, calculated by some other means (i.e. ab-initio). Again, an analytical expression for the system energy as a function of the internuclear distances is the result.

This method, when properly applied, has shown great promise in the calculation of potential energy surfaces. Whitlock et al⁽¹³⁷⁾, using this method calculated the singlet and triplet surfaces for the O/H_2 system. Their triplet surface was also considered by Schatz⁽¹³⁶⁾ to be of high quality.

The potential energy surfaces upon which the present work is based were generated using ab-initio techniques. As was intimated above this really involves two problems: the actual calculation of the points upon the surface and the prescription for choosing these points and fitting them to some reasonable function. In the following, a description of the methods used by this author are described.

b) Calculation of ab-initio points

The ab-initio points used in the construction of the PES's of this work were calculated using the MRD-CI (for Multi Reference, all single and Double excitations, Configuration Interaction) method of Buenker, Peyerimhoff and coworkers.⁽¹³⁸⁻¹⁴⁰⁾ In this method, configuration interaction is performed on the electronic configurations arising from a single SCF wavefunction. The terms "SCF" and "configuration interaction" are described below.

The Self Consistent Field (SCF) procedure is a procedure, based on the variational theorem, for the calculation of the electronic energies and wavefunctions of a system. Because of the inter-electron repulsion terms in the Hamiltonian [2], an exact analytical solution to the Schrodinger equation is impossible. Instead, the problem is solved numerically with the interelectron repulsions treated as the sum, over all electrons, of the repulsion felt by each electron in the effective field of all the others. A complete description is given in the books by Pople and Beveridge⁽¹⁴¹⁾ and McWeeny and Sutcliffe⁽¹⁴²⁾.

The variational theorem states that the expectation value of the system given by an approximate wavefunction, ψ :

$$\langle E \rangle = \langle \psi | \hat{H} | \psi \rangle$$

represents an upper bound to the "true" system energy, calculated using the exact wavefunction of the system. The SCF procedure starts off with an approximate wavefunction, given as the antisymmetrized

Hartree product of (molecular) one-electron spin wavefunctions and an "effective one-electron Hamiltonian"⁽¹⁴¹⁾, which is coupled to these one-electron wavefunctions via the effective fields felt by each electron. The wavefunctions (i.e., the molecular orbitals) are themselves composed of a linear combination of atomic functions, the so-called "basis set" of the calculation. The coefficients of the atomic functions are the variable parameters in the calculation. The solution of the eigenvalue problem results in a new set of one-electron wavefunctions and Hamiltonians. The coefficients of the atomic functions are varied until there is no further change in the resulting molecular orbitals and energies. The result is called self consistent, as the molecular orbitals thus derived are consistent with the field to which they give rise.

This procedure, from the outset, averages over the instantaneous electron-electron interactions. The "independent electron model", on which it is based, assumes that each electron is independent of all others in the system. This is not true however, the motions of various electrons are correlated, via Coulomb's Law. The error introduced by the neglect of this is therefore termed the "correlation energy". It is typically a small percentage of the total energy, but can be substantial in absolute terms. (The correlation energy of the Ne atom has been calculated⁽¹⁴³⁾ to be 0.3% of the total energy; this represents more than 10 eV. however.)

The manner in which this correlation energy is calculated is to perform another variational calculation, but on different

electronic configurations of the system (corresponding to different electronic states). The total wavefunction is cast as a linear combination of those arising from these different configurations,

Φ_i :

$$\psi = \sum_i c_i \Phi_i \quad [5]$$

and the coefficients varied so as to obtain the best (i.e. lowest) energy in the eigenvalue problem. The method is therefore labelled "configuration interaction" (CI). A good treatment of this method is given by Schaeffer⁽¹⁴⁴⁾.

The MRD-CI method has two distinctive features at the CI stage of the calculation. The calculation is based on a single SCF wavefunction, composed of occupied and unoccupied molecular orbitals. At the CI stage of the calculation, this wavefunction and up to nine additional wavefunctions, corresponding to different orbital occupancies of the SCF wavefunction, can be used as "reference" configurations (hence the "Multi Reference" in the name of the method). All symmetry-allowed single excitations from each of these reference configurations (Mains) are automatically included as Φ in the CI calculation. Double excitations are included if they lower the energy of an $n + 1 \times n + 1$ (where n is the number of Mains) test secular equation more than a specified threshold energy.

The resulting secular equation can be of enormous size, if a large number of Mains is used and the symmetry of the system is low. The second distinguishing feature of the MRD-CI method is an extrapolation procedure, whereby the energy corresponding to all possible

spin- and symmetry-allowed single and double excitations from the Mains is estimated from a subset of these. Thus, as mentioned above, a threshold energy is given as input; this determines the number of double excitations included explicitly in the variational calculation. The CI calculation is performed with this number of ϕ_i 's; it is also done for a series corresponding to higher values of the threshold energy. From these data (of CI energy vs number of configurations included) an extrapolation is made to the energy which would be obtained if all excitations were to be included in the CI calculation. (In the following chapter, this energy is referred to as the E-CI energy.) This extrapolation procedure has been described in detail (138-140,145) and its utility illustrated in

This extrapolation procedure leads to an error in the E-CI value. For the calculations to be reported herein, this extrapolation error was typically ± 0.0002 hartree (h), (i.e. 0.006 eV; 1 hartree = 27.21 eV). The threshold energy was 25 μ h for these calculations. This resulted in the inclusion of ca. 1000 configurations in the CI matrix at all points on the PES's.

After the E-CI energy had been obtained, an estimate of the residual energy lowering by quadruple excitations was made. This used the multireference analog of the Davidson⁽¹⁴⁶⁾ correction ; it was calculated as:

$$F-CI = E-CI + (1 - \sum_i C_i^2) \Delta E$$

where F-CI represents the "full" CI energy calculated in this way, the C_i are the coefficients of the Mains appearing in the E-CI

wavefunction and ΔE represents the energy difference between E-CI and the energy of the reference configurations before the CI is performed.

The correct choice of reference configurations is obviously of some importance in calculations such as this. The SCF configuration is almost always the dominant term in the final CI wavefunction. This is to be expected, as it is this wavefunction upon which all others are based. Other Mains, however, gain or lose in importance as a function of the nuclear geometry of the system. Wright and Williams (147)

have recently completed a study on the criteria by which excitations should be included explicitly in the calculation as Mains. Their conclusion was that this be done for configurations contributing more than ca. 0.5% (on the basis of the squares of the coefficients, c_i) to the final wavefunction. In the present work, the selection criterion was less stringent than this; configurations were included as Mains whose contribution was $\geq 1\%$ (on a c_i^2 basis).

The MRD-CI programs were resident on disk at the University of Ottawa Computer Centre. The calculations were carried out there, using an Amdahl (IBM compatible) computer. Each point took 3-6 minutes of CPU time on this system.

(c) Fitting of the CI Points

In a critical discussion of PES representations, Kuntz (133a) listed several criteria which must be met in order to give rise to physically realistic and reasonable surfaces. These were augmented by Wright and Gray (148) - who included restrictions so as to make the representation suitable for trajectory calculations. In (148), these

authors demonstrated the utility and quality of Rotated Morse Curve Spline (RMCS) fits to triatomic $A + BC$ type surfaces. An extension of this method was used in the present case.

The RMCS method can be explained with reference to Figure B.1.1. Consider an $A + BC$ system, at some (fixed) $A-B-C$ angle, γ . Figure B.1.1 shows a contour map of the energy as a function of the two independent distances ($A-B$ and $B-C$) for this γ . A "swing point" is now chosen in the separated atom region of the surface. This is labelled "SP" in the Figure. Let the perpendicular ray drawn from this point to the reactant asymptote be a reference ray. Now any ray drawn from SP through the interaction region is at an angle θ to this reference ray (which is at $\theta = 0$). In this nomenclature, θ becomes a measure of the "reaction coordinate"; $\theta = 0$ denotes reactants, $\theta = 90$, products and $\theta = 45$ represents equal $A-B$ and $B-C$ bond lengths.

Along any ray of constant θ , let ρ be the distance from SP. As ρ is increased, the energy is seen to be constant through the three-atom limit, drop gradually to a minimum in the interaction region (this minimum corresponds to a point along the minimum energy path for the reaction), then rise steeply up the repulsive wall as the three atoms are brought into close proximity. This behaviour of energy as a function of distance is similar to that displayed by a Morse curve. The RMCS method is based on fitting Morse curves to points at varying ρ selected along rays of constant θ . Thus for a series of rays, a series of Morse parameters - $D(\theta)$, $\beta(\theta)$ and $\rho_e(\theta)$ -

Figure B.1.1.

The rotated morse curve coordinate system. The swing point (SP), the swing angle (θ) and the distance from the swing point (r) are shown. The surface is for collinear $O(^3P)+H_2+OH+H$.

can be generated, corresponding to their values as determined from fits of points along a ray of constant θ to the Morse ⁽¹⁴⁹⁾ equation:

$$V(R_{AB}, R_{BC}, R_{AC}) = V(\gamma, \theta, \ell) \\ = D(\gamma, \theta) \{ [1 - \exp[\beta(\gamma, \theta)(\ell - \ell_e(\gamma, \theta)]]^2 - 1 \}$$

In this expression the dependence of each parameter on the A-B-C angle, γ and the swing angle, θ , has been made explicit.

The values of each parameter at different θ are then used as the nodes of a natural cubic spline; the result is a smooth and continuous function of θ . Figure B.1.2 shows some typical "spline maps" of D, β and ℓ_e vs θ , obtained in this way. Thus a smooth, continuous surface at a fixed γ can be generated. (The one shown in Figure B.1.1 is such a surface.) By following the same procedure for a series of bond angles and using the Morse parameters at each (γ, θ) as the nodes of a two-dimensional spline routine, smooth and continuous potential energy surfaces may be generated.

Using the RMCS method, the prescription for choosing the ab-initio points to be calculated becomes clear. Points are calculated at a series of geometries corresponding to values of ℓ , the distance from the swing point, for fixed γ and θ . These points should bracket the minimum of the potential along a ray of constant θ ; there should be at least three points calculated so as to provide unique solutions for the three Morse parameters in the fitting procedure. A different value of θ is then chosen and the calculations performed again. This is repeated for as many values of θ as are necessary to adequately

Figure B.1.2.

Typical spine plots of $D(\theta)$, $\beta(\theta)$ and $\lambda_e(\theta)$ vs. θ . The unsmoothed data used to generate the surface given in the previous figure is shown.

a) D vs. θ

b) β vs. θ

c) λ_e vs. θ

(c)

describe the surface. The entire procedure is then carried out for a series of bond angles.

As discussed by Wright and Gray ⁽¹⁴⁸⁾, the RMCS method can give rise to some problems. If the A-B-C bond angle goes below 60° and approaches 0° , Morse curves can no longer fit the energy as a function of ℓ and the RMCS method breaks down. ⁽¹⁵⁰⁾ This is due to the growing in of the singularity at $\gamma = 0$ along the line $RAB = RAC$. On this ray (i.e. $\theta = 45^\circ$) atom A is superimposed upon atom C; the potential is therefore infinite.

The solution to this problem ⁽¹⁴⁸⁾ lies in recognizing that for any system ABC, one of the enclosed angles must be larger than 60° . For such a system, then, three PES's can be constructed, corresponding to one of the angles A-B-C, A-C-B and B-A-C being $\geq 60^\circ$. These can then be joined together by "switching functions". The present work concerned itself with only one PES as defined in this way, however: that of $O-H-H \geq 60^\circ$.

The method as described above has recently been extended. By using "generalized Morse function" (GMF's) ⁽¹⁵¹⁾ of the form:

$$V(\gamma, \theta, \ell) = D(\gamma, \theta) \{ [1 - \exp[\beta(\gamma, \theta, \ell) \times (\ell - \ell_e(\gamma, \theta))]]^2 - 1 \}$$

where $\beta(\gamma, \theta, \ell) = \beta_0(\gamma, \theta) \times (1 + \lambda_1(\gamma, \theta)[\ell - \ell_e(\gamma, \theta)] + \lambda_2(\gamma, \theta) \times [\ell - \ell_e(\gamma, \theta)]^2)$

Wright and Williams ⁽¹⁵²⁾ obtained excellent fits to CI data (calculated using the MRD-CI method) for the first row diatomic hydrides. The fitting was done to sets of points representing 80-90% of the

dissociation energy of the diatom. The use of GMF's has also been found to yield excellent fits in three-atom RMCS surfaces ⁽¹⁵³⁾.

These studies involved the fitting of CI points calculated over a range of ℓ extending to ca. 80% of the three-atom limit. All five parameters were used in the spline routine, yielding exceptionally smooth surfaces.

The two extra parameters, λ_1 and λ_2 , cause the curvature of the GMF to change as a function of ℓ , the distance from the swing point. They have their greatest effect on the dissociation side of the GMF; the curvature of the repulsive wall is fairly insensitive to their presence. The influence of these term becomes apparent at energies above about one half of the Morse well depth. Below that energy, the standard three-parameter Morse function provides an adequate fit to the data.

In the present work, for reasons to be discussed in the next chapter, it was necessary to use a four parameter GMF (including only the term which is linear in ℓ) to describe the singlet O/H_2 surfaces. This was not required for the triplet surfaces, however, as the CI points were grouped close to the minimum of the Morse potential.

Chapter B.2: Surface Crossings and Low Temperature Rate

Enhancement in $O(^3P, ^1D) + H_2 \rightarrow OH + H$

B.2.1 INTRODUCTION

The following chapter is taken, with some modifications, from a paper entitled "Singlet-Triplet Surface Crossings and Low-Temperature Rate Enhancement for $O(^3P) + H_2 \rightarrow OH + H$ "⁽¹⁵⁴⁾. The work was inspired by two previous findings. First, in the F/OH system⁽¹⁰⁾, it had been determined that the $F + OH$ reaction takes place via a surface switching mechanism; this result has been discussed in a previous chapter. A schematic correlation diagram for the nearly thermoneutral O/H_2 system, shown in Figure B.2.1 is, apart from the different energetics, the mirror image of that for F/OH, shown in Figure 9 of⁽¹⁰⁾. That is, the analog of the surface crossing which plays a crucial role in the F/OH system occurs in the entrance channel of the O/H_2 system. This surface crossing has been discussed briefly by Howard et al.⁽¹⁵⁵⁾ (hereinafter, HML) and Whitlock et al.⁽¹³⁷⁾ (WMF). Both authors alluded to the fact that this crossing might play an important role in dynamics on these surfaces, but neither calculated the true surface crossings.

These results gained some practical significance when the Arrhenius plot (of $\log K$ vs $1/T$) for the $O(^3P) + H_2$ reaction was considered. Westenberg and de Haas⁽¹⁵⁶⁾ report a curvature in this plot for temperatures less than 400 K. The compilation of Baulch et al.⁽¹⁵⁷⁾ is also suggestive of low temperature curvature in the rate constant, especially when the recent result of Light⁽¹⁵⁸⁾ is included. However, Dubinsky and McKenney⁽¹⁵⁹⁾ show a linear Arrhenius plot over the range 347-832 K. Clearly, there is some need for further

experimental data around 300 K to fully resolve the question of low temperature rate enhancement in this reaction.

Due to the simplicity of the $O(^3P) + H_2$ system, several theoretical studies have attempted to determine $k(T)$ for the reaction. Such studies begin with a potential energy surface for the system and then do transition state theory or trajectory calculations at various values of T . These have been reviewed recently by Schatz⁽¹³⁶⁾ and by Dunning et al⁽¹⁶⁰⁾. Three different surfaces: the LEPS surface of Johnson and Winter⁽¹³³⁾, the DIM surface of WMF⁽¹³⁷⁾ and the POL-CI treatment of Walch et al⁽¹⁶¹⁾ were all described by Schatz⁽¹³⁶⁾ as giving reasonable representations of the thermal rate behaviour, especially with the inclusion of tunnelling corrections.

In spite of this apparently satisfactory situation, the results for F/OH and the accessibility and importance of the singlet-triplet surface crossings, mentioned in^(137,155) suggested that another interpretation of the low temperature curvature was possible. This interpretation holds that a non-adiabatic (i.e., not describable by a single electronic potential energy surface) transition between triplet and singlet states of the O/H₂ system could account for the curved Arrhenius plot. A full correlation diagram for this system has been given by Tsurubuchi⁽¹⁶²⁾ and reproduced, in part, by⁽¹⁵⁵⁾. A collinear approach of $O(^3P)$ to H_2 gives rise to $^3\Pi$ and $^3\Sigma^-$ surfaces; only the former correlates to ground state products, OH($^2\Pi$) and H(2S). This collinear approach is the energetically most favourable for the reaction (i.e., it has the lowest barrier). For non-collinear O-H-H

geometries (C_s symmetry group), the $^3\Pi$ surface splits into $^3A'$ and $^3A''$ components. As discussed by Walch et al⁽¹⁶¹⁾, the latter is higher in energy than the former for all but the collinear geometry, with the energy difference between them increasing as the O-H-H angle decreases. The lowest energy singlet surface correlating to ground state products is that which also correlates to ground state water (1A_1 in C_{2v}); it thus contains a deep potential well. In C_s symmetry, this surface becomes the $^1A'$ surface illustrated in Figure B.2.1.

Referring to Figure B.2.1, it is seen that the excited state reagents, $O(^1D) + H_2$, correlate to ground state products on the $^1A'$ potential energy surface; these are also the products of the ground state ($^3A''$) reaction. The deep potential well corresponding to ground state water is also shown. There is a crossing shown in the Figure between the singlet and triplet surfaces in the entrance channel. Provided that this crossing occurs below the top of the triplet barrier, a new route to products is possible, involving a switch from the triplet to the singlet surface. This route is expected to be relatively improbable, but should assume increasing importance at low temperatures.

Apart from the case of F/OH, there have been many instances of such non-adiabatic mechanisms reported (e.g.⁽¹⁶⁴⁻¹⁶⁷⁾) and theoretical calculations of the curve crossings and dynamics have been performed (e.g.⁽¹⁶⁸⁻¹⁷¹⁾). The electronic quenching of excited states of oxygen (1D)^(165,169,170) and sodium (3P)^(166,167,171) atoms has been of particular interest in this regard. In addition, Menzinger⁽¹⁷²⁾ has discussed

Figure B.2.1.

Schematic correlation diagram for the $O(^3P^1D)+H_2$ system. A surface crossing in the entrance channel is shown.

the role of curve crossings and non-adiabatic pathways in many reactive systems. The proposed mechanism is thus not entirely without precedent.

The object of this work, then, was to clarify the nature of the singlet-triplet surface crossings in the O/H_2 system, and to assess their possible importance to the kinetics of the ground state reaction at low temperatures.

B.2.2

Method of Calculation

In this study, the region of interest was the entrance channel, as the O-atom approaches the H_2 . For this reason, the calculations were carried out for the orientation O-H-H; regions of the hyper-surfaces better described by the H-O-H orientation are more relevant to the exit channel. Ab-initio calculations of both singlet and triplet surfaces were carried out at five fixed O-H-H bond angles; $\gamma = 180^\circ, 150^\circ, 120^\circ, 90^\circ$ and 60° . The calculations were performed using the MRD-CI method of Buenker, Peyerimhoff and coworkers (138-140) described in the previous chapter. All calculations involving the oxygen had that atom's 1s core (and its complement) frozen in the CI.

Two basis sets were used throughout the calculations. The first was a double zeta plus polarization (DZP) basis set of Gaussian-type orbitals with the exponents of Huzinaga⁽¹⁷³⁾ and the Dunning⁽¹⁷⁴⁾ contraction (9s 5p 1d/4s 2p 1d) on oxygen (d-exponent 0.85) and (4s 1p/2s 1p) on hydrogen (p-exponent 1.0). The second basis was used at selected "calibration points" on the surfaces (vide infra). It consisted of the above DZP basis set, augmented by bond functions placed at the midpoints of the O-H and H-H bonds. It is

denoted "BF" in the following. The hydrogen exponents were scaled by a factor of 1.2⁽¹⁷⁴⁾ in this basis so as to better describe the molecular environment. The bond functions consisted of uncontracted s- and p- type functions, with the exponents 0.35 for HH and 0.75 for OH. Calculations on the first-row diatomic hydride series using this DZP basis set augmented by bond functions⁽¹⁵²⁾ have yielded results in excellent agreement with experiment for dissociation energies and vibrational energy levels. A Rydberg orbital centered on the oxygen nucleus, with exponent 0.0275⁽¹⁵⁵⁾ was also included in some of the calculations of the triplet. These basis sets are given in Table B-I.

As the calculations were carried out at many bond angles, the entire calculation was performed in the C_s symmetry group. In this group, the lowest triplet surface is the $^3A''$ component of the $^3\Pi$ (for collinear surfaces) state⁽¹⁶¹⁾. The lowest singlet surface is that which correlates to ground state water in C_{2v} symmetry; this is a $^1A'$ state in C_s . These two ($^3A''$ and $^1A'$) surfaces were the ones calculated in this study.

For each of the five fixed bond angles, RMCS surfaces were constructed for the singlet and triplet, as described in the previous chapter. The triplet surfaces were based on twelve values of θ (the swing angle): $\theta = 0^\circ, 30^\circ, 35^\circ, 37.5^\circ, 40^\circ, 42.5^\circ, 45^\circ, 47.5^\circ, 50^\circ, 55^\circ, 60^\circ$ and 90° . The singlet surfaces used the same values of θ , except for the omission of $\theta = 55^\circ$. Typically, 4-6 CI points, bracketing the minimum, were used along each ray of constant θ .

Table B-I (cont'd)
Basis Sets Used ...

<u>orbital:</u>	DZP		BF		BF+R	
	exponent	coefficient	exponent	coefficient	exponent	coefficient
<hr/>						
Bond Functions						
OH: S & P			0.75	1.0	0.75	1.0
MM: S & P			0.35	1.0	0.35	1.0

A total of 500-600 points were calculated, over all surfaces.

The points along each Θ were fitted to the generalized Morse function by a non-linear least squares routine. For the triplet surfaces, the value of λ in the expression for β :

$$\beta = \beta_0 (1 + \lambda (1 - e^{-\lambda}))$$

was zero throughout. For the singlet surfaces, it was necessary to allow λ to vary in order to give the correct dissociation limit. As discussed by Schinke and Lester (SL) ⁽¹⁷⁵⁾ and Sorbie and Murrell ⁽¹²²⁾, as the HH bond length is increased, at large $O(^1D) - H_2$ distances, there is a surface crossing onto the repulsive triplet surface corresponding to the three ground state atoms. This is shown in Figure B.2.2. SL corrected their singlet surface by grafting an exponential function onto their Morse curve for H-H distances larger than $1.1 \text{ \AA}$.

It was desired in this work to use a single function to describe the entire surface. A three parameter Morse function, with the ground state atoms as the zero of energy, was found to give a good fit to the calculated points for $\Theta > 50$. For $\Theta < 45$, however, it was not flexible enough to fit the points and give the correct dissociation limit. A four parameter Morse function was adequate for this purpose, however. Figure B.2.2 shows the SL approach and the one taken herein.

The behaviour of λ , on the singlet surface, was examined as a function of Θ . It was found to approach zero for $\Theta > 50$, as stated above. For $\Theta < 50$ it did not exhibit entirely smooth behaviour as a

Figure B.2,2.

H_2 potential curve at large $O(^1D)-H_2$ distances. At $R_{HH}=1.7$ Å, a crossing occurs onto the repulsive curve corresponding to ground state atoms. The dashed lines show two approaches to enforcing the correct dissociation limit. Long dashes: SL connection formula. Short dashes: four-parameter morse fit (used herein).

function of Θ . There was a considerable amount of "noise" shown in plots of λ vs. Θ . This is to be expected, as the parameter describes the large- R portion of the Morse curve and very few points were calculated in this region. For this reason, it was decided to impose a functional form which showed smooth behaviour upon the parameter. This was necessary in order to avoid great difficulties in the splining procedure. Figure B.2.3 shows the chosen dependence of λ upon Θ and the "raw" points for a representative ray.

Thus for a given (γ, Θ) on the calculated surfaces, the non-linear least squares routine provided values of D , β and λ_e ; for the singlet surfaces, the value of λ was determined from the form shown in Figure B.2.3. Additional values of these parameters were generated in the non-interaction regions $\Theta = 10^\circ, 20^\circ, 70^\circ, 80^\circ$ by the method given in Wright and Gray⁽¹⁴⁸⁾. The arrays $D(\Theta)$, $\beta_0(\Theta)$, $\lambda_e(\Theta)$ and $\lambda(\Theta)$ were interconnected using natural cubic splines with the parameter values as nodes. The splining procedure occasionally gave rise to small, unphysical oscillations in the spline; in this case the data were manually smoothed to remove these oscillations. The data adjustments required were always small, however. A two-dimensional splining routine then interconnected the parameter arrays: $D(\gamma, \Theta)$, $\beta_0(\gamma, \Theta)$, $\lambda_e(\gamma, \Theta)$ and $\lambda(\gamma, \Theta)$, yielding the continuous singlet and triplet surfaces.

A scaling procedure was next carried out on these surfaces. The scaling was based on calibration points calculated using the larger (i.e. BF and $BF + R$) basis set. This allowed the general topography of these surfaces to be obtained from the DZP calculation,

Figure B.2.3.

Imposed form of λ (fourth parameter in four-parameter morse fits) as a function of swing angle, θ . The circles are the values calculated for $\gamma=60^\circ$.

while improving the energetics (well depths, barrier heights, etc) with scaling factors. The method was adapted from that of Wright and Gray ⁽¹⁴⁸⁾. First, some "critical point" (either a saddle point or a well minimum) was established for each γ from the DZP calculations. These geometries were then used to calculate points using the larger basis set. At bond angles $\gamma' = 180^\circ$ and 150° , two bond functions were used, between the OH and HH bonds. At smaller angles, an additional bond function was introduced between the O-atom and the farther H-atom. The values for the diatomic energies, ⁽¹⁵²⁾ using this basis set, are quite accurate; using them, the scaling was done as follows:

For a surface with a barrier, the crest of which appears at α , the scaling was done from reactants ($\theta = 0$) and products ($\theta = 90$) toward α . The shift in the $\theta = 0$ asymptote is: $D_{bf}(0) - D(0)$, where $D_{bf}(0)$ is the (Morse) well depth at $\theta = 0$ in the larger basis set and the unsubscripted D-value refers to the DZP result.

Let $D'(\theta) = D(\theta) + D_{bf}(0) - D(0)$, i.e. the well depth shifted to the new asymptote. The relative well depth $D'(\theta) - D(0)$ is then scaled by a multiplier to give the more accurate barrier height; the result for $\theta \leq \alpha$ is:

$$D''(\theta) = D'(0) + (D'(\theta) - D'(0)) \cdot (D_{bf}(\alpha) - D_{bf}(0)) / (D(\alpha) - D(0))$$

For $\theta > \alpha$, the terms for $\theta = 0$ are replaced by those at $\theta = 90$. In the case of potential wells, the sign before the first bracket is reversed. These scaled D-values were then used with the other (unscaled) Morse parameters to generate the scaled triplet and singlet surfaces.

B.2.3

RESULTS AND DISCUSSION

(a) Description of Selected Calculations

The swing point energy, corresponding to the separated atom limit $O(^3P) + 2H(^2S)$, was calculated for both the DZP and BF + R basis sets and also for the latter set, but excluding the Rydberg orbital (i.e. BF only). The $H(^2S)$ energy (at the SCF level, as no CI is possible) is -0.4993 hartree (h) and -0.4976 h for the DZP and BF basis sets, respectively. The latter is somewhat higher than the former due to its molecule-optimized exponent. For $O(^3P)$, the DZP calculation gave -74.8006, -74.9128 and -74.9165 h for the SCF, E-CI and F-CI energies, respectively. One reference configuration and a selection threshold of 0 h were used in this calculation; 838 configurations were generated and selected. The BF basis gave identical results, as bond functions do not contribute to atomic energies. Inclusion of a Rydberg orbital yielded energies of -74.8997, -74.9132 and -74.9170 h for the SCF, E-CI and F-CI stages of the calculation. Again, one reference configuration was used with a zero selection threshold; 1025 configurations were generated and selected. In both cases the SCF configuration (used as the one reference configuration) contributed 97% (on a c^2 basis) to the final CI wavefunction. The swing point energy as given by these calculations is then -75.9151, -75.9117 and -75.9122 h in the DZP, BF and BFR basis sets, respectively. These values serve as the zeros of energy to which all further calculations are referred.

Tables B-II and B-III give selected results of the calculations

Table B-IISelected Points on Triplet Surface; $\gamma=180$, $\theta=42.5$ DZP Basis

$\ell(A)$	E_{ref}^a	$E\text{-CI}^a$	$F\text{-CI}^a$	configurations generated/selected	Mains
5.4	-75.8634	-76.0303	-76.0419	9650/1931	3
5.5	-75.8680	-76.0379	-76.0490	9650/2037	3
5.6	-75.8678	-76.0388	-76.0491	9650/2025	3
5.7	-75.8605	-76.0328	-76.0425	9650/2178	3

a) hartrees

Table B-III

Selected Points on Singlet Surface; $\gamma=60$, $\theta=47.5$ DZP Basis

$\ell(A)$	E_{ref}^a	$E\text{-CI}^a$	$F\text{-CI}^a$	configurations generated/selected	Mains
5.2	-75.9226	-76.1365	-76.1521	3357/1212	2
5.5	-75.9934	-76.1963	-76.2079	3357/1275	2
5.6	-75.9952	-76.1941	-76.2049	3357/1301	2
5.7	-75.9728	-76.1674	-76.1772	3357/1332	2

a) hartrees

4

4

OF / DE

2.8

3.2

3.6

4.0

2.5

2.2

2.0

1.8

1.6

x

for the triplet surface, at $\gamma = 180$, $\theta = 42.5$ (the minimum barrier on this surface) and the singlet surface, at $\gamma = 60$, $\theta = 47.5$ (minimum potential on singlet). Tables B-IV and B-V display the Morse parameters calculated from these data for the triplet and singlet respectively. The quality of the fit to the data is seen to be quite good; the maximum deviation is 0.01 eV for the triplet along this ray and also 0.01 eV for the singlet. Tables B-VI and B-VII show the Morse parameters for the entire triplet ($\gamma=180$) and singlet ($\gamma=60$) surfaces.

(b) Potential Energy Surfaces

Results from the triplet calculation and for the diatomic limits are shown in Tables B-VIII-X and Figures B.2.4 and B.2.5. Table B-VIII gives the geometries and energies of the two diatomics and the saddle point at $\gamma = 180$ (collinear). Both diatomic bond lengths are seen to be ca. 0.02 Å greater than experiment when calculated with ^{the} DZP basis set. Using this basis, the calculated binding energies are lower than experiment; the DZP calculation recovers only 94% and 89% of the binding energy for H_2 and OH, respectively. The larger basis yields 100% and 99% of the experimental values. However, as the energies alone were subjected to the scaling procedure, the calculated bond lengths are in error by the stated amount.

The endoergicity (ignoring zero point energy - zpe) of the reaction

is seen to be 8.3 kcal/mol in the DZP basis and 3.9 kcal/mol for

Table B-IVMorse Fits for Triplet Surface at $\gamma=180$, $\theta=42.5$

$\ell(A)$	V_{input}^a	$V_{\text{calc.}}^a$	D^a	$B(A^{-1})$	$\ell_e(A)$
5.4	-3.45	-3.46			
5.5	-3.64	-3.63			
5.6	-3.65	-3.66	3.67	1.63	5.569 _e
5.7	-3.47	-3.46	(.01)	(.07)	(.004) ^b

a) Energies in eV

b) Error on parameter

Table B-V

Morse Fits for Singlet Surface at $\gamma=180$, $\theta=47.5$

$\ell(A)$	V_{input}^a	$V_{calc.}^a$	D^a	$B(A^{-1})$	$\ell_e(A)$	$\lambda(A^{-1})^c$
5.2	-6.45	-6.45				
5.5	-7.97	-7.97	7.996	1.730	5.536	-0.120
5.6	-7.89	-7.89	(.001)	(.003)	(.0004) ^b	
5.7	-7.13	-7.13				

a) Energies in eV

b) Error on parameter

c) Read from Figure B.2.3

Table B-VI
Scaled Morse Parameters for Triplet, $\gamma = 180$

θ	$D(\text{eV})$	$\beta(\text{\AA}^{-1})$	$\ell_e(\text{\AA})$
0	4.75	2.03	4.24
10	4.75	2.00	4.30
20	4.75	1.91	4.51
30	4.75	1.76	4.90
35	4.68	1.63	5.18
37.5	4.55	1.55	5.33
40	4.36	1.52	5.46
42.5	4.18	1.58	5.57
45	4.27	1.64	5.54
47.5	4.42	1.79	5.40
50	4.51	1.86	5.23
55	4.57	1.99	4.90
60	4.58	2.11	4.64
70	4.58	2.30	4.27
80	4.58	2.41	4.07
90	4.58	2.45	4.01

Table B-VII
Scaled Morse Parameters for Singlet, $\gamma = 60$

θ	$D(\text{eV})$	$\beta_0 (\text{\AA}^{-1})$	$\ell_e (\text{\AA})$	$\lambda (\text{\AA}^{-1})$
0	2.56	2.87	4.24	-0.612
10	2.56	2.83	4.30	-0.800
20	2.56	2.70	4.51	-0.800
30	2.56	2.45	4.90	-0.600
35	2.68	2.41	5.17	-0.415
37.5	3.25	2.16	5.33	-0.310
40	4.49	1.79	5.51	-0.240
42.5	6.47	1.58	5.61	-0.200
45	8.38	1.62	5.63	-0.150
47.5	8.90	1.73	5.54	-0.120
50	7.84	1.82	5.34	-0.090
60	4.87	2.09	4.64	-0.020
70	4.58	2.28	4.27	0.000
80	4.58	2.40	4.08	0.00
90	4.58	2.43	4.01	0.00

Table B-VIII

Geometry and energy of the swing point, diatomics, and triplet
 barrier (at 180°) obtained with the DZP and BF basis sets

Species	$R_{OH}(Å)$	$R_{HH}(Å)$	Rel. F-CI DZP	Energy(eV) BF	expt.
$O(^3P) + 2H(^2S)$			0.00	0.00	0.00
$O(^3P) + H_2$	-	0.760	-4.47	-4.75	-4.747
$OH(^2\Pi) + H$	0.990	-	-4.11	-4.58	-4.63
$3A''$ barrier	1.24	0.89	-3.67	-4.18	-

the BF + R basis set. The latter value is in good agreement with the "experimental" (corrected for zpe) value of 2.9 kcal/mol. The scaling reduces the barrier height (with respect to reactants) from 18.5 (DZP) to 13.2 (BF + R) kcal/mol, agreeing excellently with the best theoretical estimate of 13.4 kcal/mol⁽¹⁷⁶⁾

Table B-IX compares the saddle point properties (energy and geometry) calculated herein with those given by other recent calculations. The ab-initio calculations all place the barrier somewhat early along the reaction coordinate (i.e., $\theta < 45$). The transition state geometry determined in this work is slightly closer to reactants than the other ab-initio calculations, but there is, in general, good agreement.

The following Table (Table B-X) presents the barrier location and energy for each of the five triplet surfaces. The results are given for all three basis sets: DZP, BF and BF + R. The BF calculations included only two bond functions - those between the HH and the shortest OH bond. As γ decreases, it is apparent that this treatment is not sufficient. For $\gamma > 120$, the BF + R basis clearly gives superior results. These were therefore the values of the "critical points" used in the scaling procedure. The question of how much of this superiority is due to the third bond function and how much to the presence of the Rydberg orbital (cited by HML⁽¹⁵⁵⁾ as being necessary to describe the C_{2v} triplet HOH) was not explored in this work. The barrier heights given by the BF + R calculation are in reasonable agreement with those on the SL hypersurface⁽¹⁷⁷⁾, also shown in the Table.

Table B-IX

Triplet barrier height and geometry for linear OHH, from various calculations. The barrier height is with respect to $O(^3P) + H_2$.

Authors	Type	$R_{OH}(A)$	$R_{HH}(A)$	Barrier (kcal/mol)	Ref
Present	MRD-CI	1.20	0.91	13.2	
HML	FO-CI	1.15	0.95	14.0	155
SL	CI-fit	1.20	0.94	13.8	177
Walch et al.	POL-CI	1.23	0.92	12.5	161
Jacquet et al.	CEPA-CI	1.15	0.95	19.3 ^(a)	176
Whitlock et al.	DIM	1.06	1.09	13.4	137
Johnson et al.	LEPS	1.2	0.95	12.5	133

a) Extrapolated value given by these authors is 13.4 kcal/mol.

Table B- X

³A" barrier height and location vs. O-H-H bond angle γ

γ (deg.)	$R_{OH}(A)$	$R_{HH}(A)$	Barrier height(kcal/mol)			SL (a)
			DZP	2-BF	3-BF+R	
180	1.20	0.91	18.5	13.2	-	13.8
150	1.17	0.94	18.5	13.2	-	15.0
120	1.19	0.98	22.1	16.6	15.8	17.6
90	1.22	1.04	31.4	27.1	23.3	25.7
60	1.22	1.23	50.0	47.7	38.1	42.0

a) Reference 177.

Figure B.2.4.

Scaled and unscaled collinear triplet surfaces.

- a) Unscaled surface. The contours are at -4.0, -3.5, -3.0, -2.5 and -2.0 eV.
- b) Scaled surface. The contours are at -4.5, -4.0, -3.5, -3.0, -2.5 and -2.0 eV.

Figure B.2.5.

Scaled triplet surfaces for the remaining bond angles. The contours are at -4.5, -4.0, -3.5, -3.0, -2.5 and -2.0 eV.

a) $\gamma = 150$

b) $\gamma = 120$

c) $\gamma = 90$

d) $\gamma = 60$

Figure B.2.4 shows the scaled and unscaled triplet surface at $\gamma = 180$. As expected, the qualitative features of the surface are unaffected by scaling, but the energetics are better described. Figure B.2.5 displays the scaled surfaces for the remaining four triplet bond angles. The growth of the barrier height with decreasing bond angle and the overall smoothness of these surfaces is evident from the plots. The barrier location is seen to shift from reactants towards products as γ becomes smaller. This is evident as well from the geometries given in the previous Table. This shift manifests itself as an increase in the H-H bond length at the barrier crest, as the O-H distance at this point stays fairly constant. This will be seen to play an important role in the surface crossings.

The corresponding results for the $^1A'$ surfaces are given in Table B-XI. The first line of this Table shows the reagent $O(^1D) + H_2$ energy at large separation. In the BF basis, this lies 2.56 eV below ground state atoms (i.e. the swing point). As before, the barrier crests or well minima were calculated from the DZP results (columns 2 and 3 of the Table) and these geometries used to calculate the BF scaling points. A small barrier of ca. 5 kcal/mol at near-collinear geometries is calculated in both basis sets. The HH bond at the crest of this barrier is constant near 0.76 Å. This barrier is found in the entrance channel, at large O - H₂ distances. It is seen to shrink gradually as γ decreases and to be absent for $\gamma < 100$. In its place, a deep potential well grows in. A barrier to the collinear reaction was

Table B-XI

Geometries and energies on the $1A'$ surface, in both basis sets. The F-CI energies are obtained using the BF basis set.

γ	Type ^a	$R_{OH}(A)$	$R_{HH}(A)$	F-CI(BF (a.u.))	Rel. Energy (eV) ^b DZP	BF
180	A	5.0	0.76	-76.0065	-2.28	-2.56
180	B	1.75	0.76	-75.9983	-2.10	-2.34
150	B	1.75	0.77	-76.0003	-2.09	-2.40
120	B	2.19	0.75	-76.0001	-2.16	-2.39
90	W	0.93	1.04	-76.1468	-5.58	-6.38
60	W	0.92	1.21	-76.2403	-8.02	-8.93
HOH ^c	W			-76.2772	-8.99	-9.94

a) A = diatomic asymptote, B = barrier, W = well.

b) Relative to $O(^3P) + 2H(^2S)$.

c) Equilibrium geometry for H_2O , with angle HOH = 104.5° .

given by both SL⁽¹⁷⁵⁾ and WMF^(137,178). These calculations yielded barrier heights of about 1 kcal/mol, however, somewhat less than the value determined herein.

From the results listed in this and the previous Table, several features of interest may be derived. The $O(^3P)/(^1D)$ energetic splitting is 2.19 eV in both DZP and BF basis sets. This value is 0.225 eV higher than the experimental value of 1.965 eV and will cause some distortion of the surface crossings, as the $O(^1D)$ energy starts out being too high by this amount. However, the only other full calculation of both singlet and triplet surfaces, that of HML⁽¹⁵⁹⁾ gave an energy difference of 2.30 eV between singlet and triplet O-atoms. The erroneous value calculated for the splitting may arise from the fact that the basis set is optimized for ground state atoms, though this point was not pursued.

The exoergicity of the $O(^1D)/H_2$ reaction is calculated to be 1.83 eV in the DZP basis and 2.02 eV for the BF calculation. These are to be compared to the experimental value of 1.85 eV. The very good agreement given by the DZP basis is the result of a fortuitous cancellation of errors in the $O(^1D)/O(^3P)$ splitting and the OH energy. Use of the correct value for the latter in the BF basis restores the error in the splitting and thus gives rise to an erroneous exoergicity. Though this would be expected to affect the reaction dynamics on this surface, no new errors are introduced insofar as the surface crossing calculation is concerned.

The last line of Table B-XI shows the energy calculated for

ground state water, using both basis sets. The DZP calculation gives a value of 8.99 eV for the well depth, recovering 89% of the experimental value of 10.08 eV. The BF basis does much better; the calculated energy of 9.94 eV represents 99% of the well depth for water.

Figure B.2.6 shows the scaled and unscaled surfaces for the singlet, at $\gamma = 60$. Once again, the scaling is seen not to have affected the qualitative features of the surface, but to have improved the energetics. Figure B.2.7 shows the scaled results for the remaining singlet bond angles. As was given in Table B-XI these show a barrier for $\gamma \leq 120$, which gradually diminishes in height as γ decreases. For the more highly bent geometries ($\gamma = 90, 60$), this barrier has completely vanished and a deep well has formed. At $\gamma = 60$, this is 8.93 eV below the swing point energy, representing 90% of the H_2O minimum. This well is centred toward the exit channel, in contrast to the triplet barriers which were located in the entrance channel. The singlet surfaces are all strongly attractive; that is, most of the reaction exoergicity is released prior to $\theta = 45$, while the reagents are approaching one-another⁽⁶²⁾. As the bond angle is decreased, the surfaces become increasingly attractive, a feature which will be shown to be of importance to the surface crossings.

(c) Surface Crossings

Surface crossings occur in those regions of space where the singlet and triplet systems share a common energy and geometry.

Figure B.2.6.

Scaled and unscaled singlet surfaces at $\gamma=60$.

- a) Unscaled surface. The contours are in 1.0 eV increments from -7.5 to -1.5 eV, with an additional contour at -2.0 eV.
- b) Scaled surface. The contours are in 1.0 eV increments from -8.5 to 1.5 eV, inclusive.

Figure B.2.7.

Scaled singlet surfaces for the remaining bond angles.

- a) $\gamma = 90$. The contours are at -6.0, -5.5, -4.5, -3.5, -2.5 and -1.5 eV.
- b) $\gamma = 120$. The contours are in 0.5 eV increments from -4.5 to -1.5 eV, inclusive.
- c) $\gamma = 150$. Same contours as b).
- d) $\gamma = 180$. Same contours as b), with the addition of a contour at -2.36 eV, to better define the barrier.

There are many regions in which this takes place; not all are of interest. As the reaction product is the same for both states of the reactant O-atom, the surfaces become identical late along the exit channel. Also, because of the enforced common zero of energy, areas of hyperspace approaching the three atom limit are the same for both. These crossing regions occur either after the triplet barrier or high in energy and so are not of interest to this study. The following discussion is concerned with crossings in the entrance channel or near the transition-state region of the triplet surface.

A simple but illuminating picture of the region in which these crossings occur can be constructed as follows: For a fixed bond angle the minima of energy (i.e. the D-values from the Morse fits) are plotted for each of the triplet and singlet, as a function of swing angle, θ . Figure B.2.8 shows such plots for bond angles 180° , 120° and 90° . To properly interpret these plots, it should be stressed that the points of intersection as shown on them will yield only the minimum possible crossing energies. This is because the minimum energy paths (MEP) through space are different for the two systems. As the D-values correspond to the energy along the minimum energy paths, the intersections shown in the Figure will indicate only the region in which true crossings occur. (For identical MEP's, this point is exact.) This loss of precision in locating the crossings, however, is compensated for by rendering the crossings more readily visualizable along a single reaction path.

Two general trends can be seen from inspection of Figure

Figure B.2.8.

Relative energy vs. swing angle for the singlet (upper curve) and triplet surfaces at various bond angles. The energy is calculated from the D-values, given by the (scaled) morse fits. The trend in the crossings towards higher energies and smaller θ as the bond angle decreases is clear.

- a) $\gamma = 180$
- b) $\gamma = 120$
- c) $\gamma = 60$

[a]
CRØSSINGS
 $\gamma = 180$

(c)

CROSSINGS

$\gamma = 60$

B.2.8. First, as the bond angle is decreased, the points of intersection of the singlet and triplet curves move towards reactants - farther into the entrance channel. Thus, for $\gamma = 180$, the collinear geometry leads to no intersections until quite far into the product channel. This is where the surfaces become tangent, as the same products are formed in each case. With decreasing bond angle, the singlet surfaces become increasingly attractive, as mentioned earlier. In addition, the triplet barrier shifts slightly in the direction of the exit channel. Thus at $\gamma = 120$, the reaction exoergicity is released earlier along the singlet surface, resulting in an earlier surface crossing than for the collinear geometry. At this angle, the intersection occurs at a region very close to the triplet barrier (recall, however, that these plots show only the minimum possible crossing energies). By $\gamma = 60$, the crossing has moved well into the entrance channel.

The second trend obvious from these plots is the increasing energy of the crossing region as γ is reduced. This effect is due to the increasing barrier height on the triplet surfaces. At $\gamma = 120$, Figure B.2.8b implies that the crossing will occur at an energy equal to or greater than the barrier height at that angle. This is given in Table B-X as being about 16 kcal/mol. At $\gamma = 60$, however, the minimum crossing energy is seen to have increased to ca. 18 kcal/mol. Since the energy of the surface crossing was the central question of this work, the region around $\gamma = 120$ was of particular importance.

A detailed search for the actual surface crossings was then

carried out, using the continuous singlet and triplet surfaces generated previously. The object of this search was to pinpoint any low energy crossing region(s) which occur prior to the triplet barrier. This was done as follows:

A rough scan was first performed, between $\gamma = 60$ and $\gamma = 175$, using an increment of 5° in γ . For each γ , the swing angle, θ , was incremented by 2.5° , from $0 - 52.5$ and ℓ was incremented by $0.02 \text{ \AA}$, over the full range. This mesh covered all regions of interest in (γ, θ, ℓ) space. At each (γ, θ, ℓ) , the energies of singlet and triplet were computed and the difference in energy calculated. This procedure served to locate the regions of interest to this study. In these regions, a further calculation was undertaken, but with increments in (γ, θ, ℓ) of 1° , 1° , and $0.02 \text{ \AA}$, respectively. All regions in which the energy difference was less than 0.02 eV were calculated using this finer mesh.

The results confirmed the qualitative picture obtained from Figure 8.2.8. They are displayed, for $\gamma = 150, 120$ and 90 , in Figure 8.2.9. For each angle, the corresponding triplet contour plot is shown, with the crossing seams (solid lines) and the singlet MEP (dashed lines) superimposed upon it. The crossing seams represent the regions in (ROH, RHH) space in which energy differences of less than 0.02 eV were obtained from the above calculation.

When the MEP of the singlet is shown on the triplet contour plots, as in Figure B.2.9, it becomes clear that plots such as those given in Figure B.2.8 can be misleading, and should be interpreted with caution. As the geometry becomes more bent, the singlet MEP is

Figure B.2.9.

Surface crossings at three bond angles, shown on the triplet surface contour maps. The crossing seams are shown as solid lines; the singlet MEP as a dashed line. The displacement of the crossing seams towards higher energies and "earlier" locating along the reaction coordinate as the bond angle is decreased is again clearly shown.

- a) $\gamma = 150$
- b) $\gamma = 120$
- c) $\gamma = 90$

seen to deviate increasingly from that of the triplet. (The latter is not shown, but is obvious from the shape of the contours.) The reagents approach one another much more closely on the singlet than on the triplet surfaces. The geometries along the respective MEP's therefore become quite different, especially around the region of the triplet barrier.

The results displayed in Figure B.2.9 show more quantitatively the general trends of Figure B.2.8. At $\gamma = 150$, there are no crossings found until the exit channel is reached and the surfaces become coincident. At $\gamma = 120$, a seam appears very slightly after the triplet barrier crest. It intersects the triplet MEP near the saddle point, at an energy 15.0 kcal/mol above the ground state reactants. This energy is very close to, but slightly above the calculated barrier height at $\gamma = 180$ (13.2 kcal/mol), which is the minimum barrier to reaction. Additional crossing seams are seen in the exit channel, parallel to, but at somewhat higher energy (ca. 0.2 eV) than the triplet MEP. At the more highly bent geometry, $\gamma = 90$, the crossing seams have moved well into the entrance channel, prior to the triplet barrier, but at an energy ca. 20 kcal/mol above reactants. This energy is well in excess of that of the lowest triplet barrier.

The present results thus indicate that there is a trade off between energy and position along the reaction coordinate in the surface crossings. For geometries near collinear, the singlet and triplet surfaces do not cross; they become coincident late in the exit channel. This is because for these geometries, there is no potential

well in the singlet surface. As the O-H-H angle is decreased from 180° , the singlet surfaces become more attractive. At some point, the singlet surface becomes lower in energy than the triplet. This occurs in the exit channel and is the result of the singlet surface reaching the product asymptote prior to the triplet, because of the barrier in the latter. This is seen to be the case at $\gamma = 120^\circ$, where there is a crossing of the surfaces very close to the barrier crest of the triplet. It should be noted that there is still no well in the singlet surface, however. At geometries which are farther still from collinear, the deep potential well of the singlet at bent geometries causes that surface to plummet far below that of the triplet. There is thus a crossing in the entrance channel, prior to the triplet barrier, as the reagents are still approaching one another. However, this crossing takes place at an energy in excess of that of the lowest triplet barrier. This is due to the increase in the triplet barrier height as the bond angle is diminished.

The compromise between these two effects occurs at $\gamma = 120^\circ$ ($\pm 1^\circ$ - the mesh size in the search). The crossing between the singlet and triplet surfaces at this bond angle is very close to the crest of the triplet barrier at that angle, but is not yet in the entrance channel. The energy of the crossing at this point (15 kcal/mol) is just slightly above the energy of the barrier on the collinear surface. The geometry at this point is: (RHH) = 1.00°
 $A, R(OH) = 1.15^\circ A.$

These results may be compared to those presented in two

previous studies ^(137,155) of the O/H_2 system. WMF ⁽¹³⁷⁾ performed DIM calculations of both triplet and singlet surfaces. A barrier of 13.4 kcal/mol was found by them for the triplet ($\gamma = 180$) surface,

in excellent agreement with the value reported herein.

For the C_{2v} "insertion" pathway, a barrier on the triplet surface of 31.4 kcal/mol was reported. In a brief discussion of the possibilities of singlet-triplet interaction, a figure (Figure 21 of ⁽¹³⁷⁾) very similar to Figure B.2.8 of the present work is presented of the singlet and triplet MEP's for the C_{2v} pathways. An intersection of the two curves is evident at an energy of 13.4 kcal/mol; because of this those authors suggested that the insertion route involving a surface crossing to the singlet might compete with the collinear abstractive route on the triplet surfaces. The intersection of the MEP curves does not, however, give the properties of the "true" crossing region. This was discussed at some length in the previous paragraphs. The present results suggest that, for a C_{2v} insertion mechanism, the singlet and triplet MEP's through space would be quite different, except far into the entrance and exit channels. The true surface crossing, for this approach geometry, must be higher in energy than the reported MEP crossing energy of 13.4 kcal/mol.

A similar calculation was carried out by HML ⁽¹⁵⁵⁾, using their ab-initio singlet and triplet surfaces. In their Figure 4, they show the potential energy along the C_{2v} insertion pathway. Once again, however, the H_2 bond lengths had been optimized for each position of the incoming oxygen atom. This figure is thus an MEP plot, as for Figure 21 of WMF and B.2.8 of this work.

However, to ensure that the true crossings were indeed above those implied by the MEP plots of WMF and HML, a calculation of these crossings, along the C_{2v} insertion path, was performed. This made use of the fitted HML surfaces, given by Schinke and Lester (175,177)

The same procedure was followed to find the crossings in the SL surface system as was used for the present results. The lowest energy crossing point found along the C_{2v} path on the SL surfaces lay ca 20 kcal/mol above ground state reactants. The geometry at that point is $R(HH) = 0.74 \text{ \AA}$, $R(OH) = 1.50 \text{ \AA}$. This, in the present notation, is given as $\gamma = 74$, $\theta = 39$. Thus, as is expected, the crossing lies quite far into the entrance channel, but at an energy in excess of the lowest triplet barrier. As the present potential surfaces are qualitatively quite similar to those of SL, it seems unlikely that a lower energy surface crossing exists along the C_{2v} insertion pathway than was reported in this work.

The results of this study indicate that a crossing of the $^3A''$ and $^1A'$ surfaces occurs at an energy very close to, but slightly above that of the lowest triplet barrier. This raises the question of the amount of confidence which can be placed in the CI calculation. The bond function basis set has been shown to give diatomic hydride potential curves which are accurate to within 2 kcal/mol over the entire range (152). For triatomics, extensive calculations (CI points taken up to 80% of the three atom limit) using this basis set have been performed on collinear F/H_2 , H_2O at its equilibrium geometry and the collinear $O(^3P)/H_2$ system (153). The results of the latter

calculation, performed by this author, are in good agreement with the scaled $\gamma = 180$ triplet surface, which was described above. In particular, the barrier height is found to lie 12.8 kcal/mol above reactants, compared to the 13.2 kcal/mol reported herein for the scaled DZP surface. Table BXII and Figure B.2.10 show the results of the more extensive calculation; they are to be compared to Table B-VI and Figure B.2.4b, which relate to the scaled DZP surface.

d) Conclusions

From these results it is then concluded that a surface switching mechanism, such as occurs in the exit channel of the F/OH system, is not responsible for the low temperature rate enhancement of the $O(^3P) + H_2$ reaction, as the energy of the surface crossings appears to be too high. Any enhancement which is present must therefore be due to quantum mechanical tunneling through the potential barrier, as assumed previously. It would be desirable to pursue this point somewhat farther, though, using the bond function basis set throughout, as well as a basis set for the oxygen atom which yields the experimental value for the $^3P-^1D$ energy difference.

Table B-XII
 Five-Parameter GMF Fits to Triplet Surface, $\gamma = 180^a$

θ	D^b	ℓ_e^c	β_o^d	λ_1^d	λ_2^e
0	4.750	4.552	1.999	0.115	0.182
30	4.798	5.252	1.721	0.077	0.125
35	4.755	5.552	1.606	0.113	0.150
37.5	4.677	5.708	1.566	0.079	0.111
40	4.450	5.882	1.483	0.091	0.125
42.5	4.196	6.002	1.531	-0.011	0.018
45	4.280	5.978	1.589	-0.017	0.071
47.5	4.469	5.821	1.695	-0.015	0.082
50	4.563	5.628	1.784	-0.024	0.071
55	4.581	5.272	1.905	-0.006	0.114
60	4.575	4.985	1.992	0.007	0.175
90	4.564	4.318	2.330	-0.006	0.161

a) from reference 157

b) Energy in eV

c) in Å

d) in Å⁻¹

e) in Å⁻²

Figure B.2.10.

Five-parameter GMF surface for collinear $O(^3P)+H_2 \rightarrow OH+H$, from reference 157. The contours are at -4.5, -4.0, -3.5, -3.0, -2.5, -2.0 eV, to compare to Figure B.2.4b.

Appendices

APPENDIX I

Coating of Glassware

The reagent inlet glassware was teflon-coated in the following manner: The glass to be coated was first cleaned by rinsing with 48% HF solution for about 2-5 minutes. It was then rinsed with distilled water and placed in an oven kept at 300⁰ for a few minutes, to dry. When dry, it was ~~removed~~ from the oven and allowed to cool somewhat. When the glass had cooled to ca. 50-60⁰C, it was dipped in a commercially available teflon slurry (DuPont); it was allowed to be immersed in this slurry for about a minute. It was then allowed to dry for about 3 minutes, being suspended such that the wetted surfaces were not in contact with anything. The coated piece was then replaced in the 300⁰C oven for a period of ca. 1.5 hours. Air was circulated through the oven during this time. This procedure resulted in a clear, robust teflon coating.

APPENDIX 2

The Numerical Simulation Routine

In Chapter A.3 the results of a numerical simulation of the F/NH_3 reaction, as it occurs in the present apparatus, were reported. These were used to extract the contributions to the observed HF vibrational distribution from the primary and secondary reactions. The purpose of this Appendix is to describe the simulation routine ("the simulator") more fully than was done in that chapter.

The simulator is a computer model written to simulate the processes occurring in the chemiluminescence apparatus which give rise to vibrationally excited HF. It has as its object a complete description of the low pressure experiment, based on simple physical laws. It can therefore be used to examine in detail systems exhibiting unusual results, to try to explain these. It can also be used to gain an estimate of the vibrational distributions arising from each of two reactions, when these cannot be measured in isolation. In conjunction with a series of experiments on such a system, it is a very powerful tool for the study of secondary reactions.

All processes contributing to the population of each HF vibrational level are included in the simulation. These include: formation by chemical reaction, energy transfer processes, both in the gas phase and on the inlet walls, spontaneous emission and diffusion out of the observation zone. There are six variable parameters in the model which serve to describe processes which cannot be experimentally determined. These parameters (which are

described below) are optimized by means of a non-linear least squares routine which minimizes the RMS deviation between the predicted and observed vibrational distributions and total emission intensities for a "calibration reaction":

The measured data set to which the prediction is compared consists of a series of 11 experiments, differing from one another in some experimental detail - reagent flows or injector location. By varying these experimental conditions, the effect on the observed results of changing the gas phase deactivation and reaction patterns (by varying the reagent flows), as well as the pressure in the reaction zone and the effect of wall collisions (by varying the injector position) can be explored. As all vibrational distributions and total intensities must be reproduced to within the experimental error (2% and 10%, respectively) by the calculation, this provides a stringent test of the model.

The simulation is carried out as follows: First the flow of F-atoms is calculated, from the measured precursor flow, by the use of the first parameter, Nd. This parameter represents the total number of F-atoms produced in the microwave discharge per molecule of precursor gas. Next, the initial partial pressures of F-atoms, undissociated precursor molecules and radical fragments is calculated. This conversion from flow rates to partial pressures makes use of conservation of mass, flow and the appropriate equations for the conductance of the tube carrying the atoms (tube 2) ⁽¹⁷⁹⁾. Since

both the flow rate and instantaneous conductance of the tube are known, the average bulk flow velocity is determined by the calculation, as well.

During the experiment, the molecular reagent enters the system through a radial slot at the bottom of the injector tube. It is assumed, based on the size of the slot and the (measured) pressure in the injector tube, that effusive flow conditions govern the injection of the molecular reagent into tube 2. The flux distribution of this reagent is therefore assumed to be cylindrically symmetrical about the axis of the injector with a cosine distribution in the vertical direction, peaked at the injector tip. This provides an analytic starting point for the calculation of the reagent flux at any point surrounding the injector.

The calculation of the actual value of the molecular flux depends upon the region of the inlet assembly for which the calculation is being carried out. The apparatus is divided into four regions, corresponding to: inside tube 2, but above the injector tip (region 1); inside tube 2, below the injector (region 2); inside tube 2, one mean-free-path from its end (region 3) and outside tube 2, in the low pressure region of the apparatus (region 4). To obtain the partial pressure of the molecular reagent in the first region, a conservation-of-mass-flow condition is applied at every value of the position above the injection point. At each step in the calculation, the upward flux of the molecular reagent through a plane perpendicular to the tube axis is calculated, using the cosine function computed as given above. This flux is then multiplied by the function:

$\exp(\ell/\ell_m)$, where ℓ is the distance from the injector and ℓ_m is the mean free path at ℓ , based on the partial pressures of the discharge products. This accounts for the attenuation of the molecular flux by the downward-flowing gasses. The upward flow thus calculated is equated to the downward flow of the same gas, as it is assumed that no gas escapes from the top of the tube. The resulting equation defines the instantaneous partial pressure of molecular reagent, via the appropriate conductance equations.

The molecular reagent density in region 2 and all regions below it is given as the sum of the reagent flowing downward in tube 2, plus that obtained by direct injection via the injection function, described above.

At a distance of one mean free path from the end of tube 2 (as calculated from the instantaneous partial pressures in effect at the time), region 3 (the transition region) is entered. In this region, the conductance equations are switched to those for intermediate flow in a short tube (including end effects)⁽¹⁷⁹⁾ and two additional functions are switched on. These describe the expansion of the gas mixture into the low pressure region and its approach to free-molecular velocity, from that determined by the conductance equations appropriate to regions inside tube 2; described above. Each of these functions contains one of the six parameters mentioned above.

The transition of the bulk flow velocity from that inside tube 2 (determined by the conductance equations) to that appropriate to free molecular flow (approached at some limiting

(large) distance from the end of the tube) is governed by an arctangent switching function:

$$v(\ell) = v(0) + (v_{\text{mol}} - v(0)) \times \tan^{-1} (\ell/P_v)/2\pi$$

In this expression, ℓ is the distance from the start of the transition region, at which the computed bulk flow velocity is $v(0)$; the free molecular flow velocity is denoted as v_{mol} . The parameter P_v gives the distance at which the mean axial flow velocity is half way between $v(0)$ and v_{mol} .

The expansion of the gas mixture into the low pressure region is approximated by assuming that the pressure decrease as a function of ℓ is given by a gaussian function, having the form:

$$\exp(-\ell/P_p)^2$$

in which P_p is a parameter corresponding to the value of ℓ at which the pressure has reached $1/e$ of its value at the start of the transition region. This is a great simplification of the actual expansion process, neglecting as it does such factors as the focussing effect due to flow from a long tube at low pressures⁽⁷⁵⁾ and the lateral injection of molecular reagent in the vicinity of the bottom of tube 2. These two factors have opposite effects, however, and the approximation introduced by the use of a gaussian to model the expansion seems to be acceptable.

Below the bottom of tube 2 (region 4), all processes having to do with the inlet walls are switched off. These processes involve deactivation of vibrationally excited HF by the inlet walls.

The wall deactivation of HF^+ is approximated as the sum of two processes. The first involves a $\Delta v = 1$ process, governed by a rate constant for the $v = 1 \rightarrow v = 0$ deactivation and a scaling factor, giving the v -level dependence of the wall deactivation rate. These two are used as parameters in the calculation. The second wall process is a deactivation from any given v -level directly to $v = 0$. This rate constant, which is assumed to be independent of the v -level being deactivated, constitutes the final parameter in the calculation.

These wall processes are parameterized because the accommodation of vibrational energy on surfaces is a complicated function of the exact state of the surface and the nature of the gas-surface interactions. It is thus expected to vary between experiments in the current apparatus. The single-quantum deexcitation process is assumed to scale as a small power of the v -level being deactivated. This scaling is that which is observed for collisions of HF with large, non-resonant molecules⁽⁷³⁾ and therefore seems reasonable in the current context. The $(v \rightarrow 0)$ deactivation is made independent of v -level. This process is not observed under "normal" conditions, with "clean" inlet walls. It is observed, however, in the case of the F/NH_3 experiments, in which there is a strong interaction between the HF and the wall coating. Under these conditions of strong interaction with the walls, a strong dependence of the deactivation rate upon the initial v -level is not expected.

These six parameters, as well as the measured reagent flow rates (from which reagent densities are calculated) and published

values of all other (reaction and deactivation) rate constants are used in the rate equations of the simulation. The detailed rate constants for formation of individual HF v-levels are calculated from the total rate constant and the vibrational distribution observed in the experiments, under the lowest-flow, lowest-injector-location conditions conducive to observing a signal. As mentioned above, the six parameters are optimized using the results from a series of 11 $F + H_2$ calibration experiments. Thus there is a total of 44 data values to be reproduced by the six parameters (33 corresponding to the vibrational distributions and 11 to the relative total emission intensities).

The steps in each calculation are as follows: Beginning at the top of tube 2, where the concentration of molecular reagent is negligible, a sample of gas is followed downwards. The rate equations, which include all processes contributing to the product vibrational distributions, are integrated at every step. At the time when the sample reaches the light-collection optics, a summation of the infrared emission, weighted by the efficiency function of the optics (74), is begun. This summation continues until the sample passes out of view of the mirrors. The resulting sum gives the vibrational distribution and total emission intensity for comparison to the measured values. In addition, the final total pressure, flow velocity, elapsed time and mass conservation are printed.

The calculation is initialized using a fourth order Runge-Kutta procedure, then carried out by a sixth order Adams-Moulton predictor-corrector routine. The stiffness ratio of the rate equations is less than 10^6 , hence this procedure provides

adequate stability. The time step used in most calculations is 2×10^{-7} sec; halving this does not affect the results.

The optimization of the parameters is carried out in a cyclic iterative procedure. The complete dataset is simulated and the RMS deviation between the measured and calculated values obtained. One of the parameters is then varied slightly and the calculation repeated, yielding another RMS deviation. This is repeated again, but in the opposite direction; the result is a set of three parameter values and the corresponding RMS deviations from the measured data. A parabola is computed through the three pairs of values. The minimum of this parabola is used to set the value of the parameter being optimized. The calculation then moves on to the next parameter, where the entire procedure is repeated. In this way, the entire parameter set can be optimized.

The calculation is performed on an LSI 11/23 - based system, equipped with hardware arithmetic. A single calculation of the dataset (eleven F/H₂ experiments) takes ca. 100 minutes on this system. A complete optimization requires about a week.

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