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DYNAMICS OF INSERTION REACTIONS OF O(¹D)

by

ERIK KRUUS

A thesis submitted to
the Faculty of Graduate Studies and Research
in partial fulfillment of
the requirements for the degree of

Doctor of Philosophy

Department of Chemistry

Carleton University

Ottawa, Ontario

February 7, 1989

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in partial fulfillment of the requirements
for the degree of Doctor of Philosophy

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Abstract

The use of basis sets involving bond functions for H_2 and H_3 potential energy surfaces was studied. Bond function bases provided an economical method to obtain potential surfaces of intermediate accuracy, with two excellent choices of basis set for H_2 being BF1 (a scaled DZP nuclear basis augmented by one set of optimized sp bond functions) and BF2 (a scaled TZPP basis with two sets of optimized sp bond functions.) Both BF1 and BF2 bases were found to provide reasonable descriptions of the global energetics of the H_3 surface; however, BF2 showed decreased local variation from parallelism to the "true" H_3 surface.

Time-resolved measurements of the infrared chemiluminescence resulting from reactions of $O(^1D)$ with $HR = HCl, HBr, H_2S$ and CH_4 were recorded using an interferometer. The initial vibrational distribution of the vibrationally excited product OH was determined for each of these reactions. The dynamics of these reactions was in each case explained as an insertion of $O(^1D)$ into the HR bond. Because of the asymmetric potential energy surfaces involved and the large difference in mass between H and R groups, this insertion would more strongly excite the asymmetric stretch of the intermediate HOR than for the $O(^1D) + H_2$ reaction. This increased stretching of the triatomic complex ultimately resulted in increased vibration of the OH product. The results indicated that an upper limit of $\sim 60\%$ of the reaction exothermicity was converted into vibrational energy of the product OH in each reaction.

The normalized initial vibrational distributions of the $OH^\dagger$ product of the $O(^1D)$ reactions with HCl and HBr were $P_{OH}(v=1-4) = (4\pm 2): (19\pm 2): (42\pm 3): (34\pm 3)$ and $P_{OH}(v=1-5) = (8\pm 3): (11\pm 3): (18\pm 2): (31\pm 4): (32\pm 5)$ respectively. The presence of primary HCl and HBr products suggested that the lowest excited singlet and triplet states

of HOCl/HOBr may have been involved. A secondary V-V process from $\text{OH}^\dagger$ populating $\text{HCl}(v=1)$ and $\text{HBr}(v=1)$ was noted.

Measurements involving $\text{O}(^1\text{D})$ reactions with H_2S and CH_4 showed the initial vibrational distributions to be $P_{\text{OH}}(v=1-5) = (8\pm3): (11\pm3): (18\pm2): (31\pm4): (32\pm5)$ and $P_{\text{OH}}(v=1-4) = (22\pm5): (38\pm4): (30\pm3): (10\pm3)$ respectively.

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I thank those who helped me along during my graduate work. Foremost among these are my two supervisors, Drs. Jim Wright and Jim Sloan. Dr. Wright, my "theoretical" supervisor had to cope with my impatience and skepticism and, in spite of such obstacles, managed to guide me towards a more careful and thorough approach to science. Dr. Sloan, my "experimental" supervisor, renewed my enthusiasm for science by providing a challenging and independent project for me, while always being there to help, consult or query when difficulties arose. Thanks, Jims, it was *fun* being part of your teams.

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Table of Contents

	Page
Acceptance Sheet	ii
Abstract	iii
Acknowledgements	v
Table of Contents	vi
List of Tables	vii
List of Figures	viii
 CHAPTER 1: <i>Use of Bond Functions in CI Calculations</i>	
1.1 Introduction: Bond Functions, H ₂ and H ₃	1
1.2 Method of Calculation	4
1.3 Results and Discussion: H ₂	6
1.4 H ₃ : the Rotated Morse Curve Method	19
1.5 Results and Discussion: H ₃	19
1.6 Conclusions	43
 CHAPTER 2: <i>Introduction to O(¹D) Reactions</i>	
2.1 Overview of O(¹ D) Reactions	46
2.2 General Dynamics of O(¹ D) + RH Reactions	61
 CHAPTER 3: <i>General Experimental Description</i>	
3.1 General Considerations	70
3.2 Specifics of the Time-Resolved Accessory	73
3.3 Overview of the Data Acquisition Software	78
3.4 General Experimental Aspects	82
3.5 Analysis of the Spectra	88
 CHAPTER 4: <i>The Reaction O(¹D) + HCl → OH + Cl</i>	
4.1 Introduction: O(¹ D) + HCl	90
4.2 Experimental	99
4.3 Results and Discussion	100
4.4 Mechanistic Hypotheses	118
 CHAPTER 5: <i>The Reactions of O(¹D) with HBr, H₂S and CH₄</i>	
5.1 Introduction: O(¹ D) + HBr	127
5.2 O(¹ D) + HBr Experimental Details, Results and Discussion	129
5.3 Introduction: O(¹ D) + H ₂ S	137
5.4 O(¹ D) + H ₂ S Experimental Details, Results and Discussion	141
5.5 Introduction: O(¹ D) + CH ₄	149
5.6 O(¹ D) + CH ₄ Experimental Details, Results and Discussion	152
 CHAPTER 6: <i>Summary and Conclusions</i>	158
 REFERENCES	162

List of Tables

TABLE	DESCRIPTION	PAGE
1	H ₂ Cl energies calculated using the DZ*P + bf(sp) basis as a function of internuclear distance and exponents coefficient	7
2	Parameters of different bases for H ₂	17
3	Rotated Morse Curve Fits for Collinear H ₃ Surfaces	21
4	Characteristics of Basis Sets used in H ₃	31
5	Average Difference in Energy Between RMCS H ₃ surfaces and Liu's Original Data Points.	31
6	Transition State Properties	33
7	Cl Energies for Linear Equidistant H ₃	42
8	BSSE for the BF1 Basis Set	42
9	Populations of Rovibrational Levels; OH Product of the O(¹ D) + HCl Reaction	103
10	Populations of Rovibrational Levels; HCl Product of the O(¹ D) + HCl Reaction	108
11	Populations of Rovibrational Levels; OH Product of the O(¹ D) + HBr Reaction	132
12	Populations of Rovibrational Levels; OH Product of the O(¹ D) + H ₂ S Reaction	142
13	Populations of Rovibrational Levels; OH Product of the O(¹ D) + CH ₄ Reaction	155

List of Figures

FIGURE	DESCRIPTION	PAGE
1	Basis set incompleteness for H_2 for variations of the DZ* and DZ*P nuclear basis sets	8
2	Basis set incompleteness for H_2 for variations of the TZP nuclear basis set	9
3	Basis set incompleteness for H_2 for variations of the TZPP nuclear basis set	10
4	Basis set incompleteness for H_2 for variations of the TZ*P nuclear basis set	11
5	Basis set incompleteness for H_2 for variations of the TZ*PP nuclear basis set	12
6	Basis set incompleteness for H_2 for further variations of the TZ*PP nuclear basis set	13
7	GMF5 parameter $D_e(\theta)$	23
8	GMF5 parameter $I_e(\theta)$	24
9	GMF5 parameter $\beta_0(\theta)$	25
10	GMF5 parameter $\lambda_1(\theta)$	26
11	GMF5 parameter $\lambda_2(\theta)$	27
12	H_3 potential energy surfaces calculated with DZ* and (DZ* + P @ 1.00) basis sets	28
13	H_3 potential energy surfaces calculated with (DZ*P + bf(sp) @ 0.35) ("BF1") and (TZ* + PP @ 1.00 & 0.30) basis sets	29
14	H_3 potential energy surfaces calculated with the (TZ*PP + 2bf(sp) & 2.20 & 0.80) ("BF2") basis set and the analytical function of SLTH	30
15	Difference energy plot for the DZ* basis	35
16	Difference energy plot for the DZ*P basis	36
17	Difference energy plot for the DZ*P + bf(sp) @ 0.35 ("BF1") basis	37

18	Difference energy plot for the TZ*PP basis	38
19	Difference energy plot for the TZ*PP + 2bf(sp) @ 2.20 & 0.80 ("BF2") basis	39
20	Qualitative energy level diagram for the $O(^1D) + HR$ $\rightarrow OH + R\cdot$ reaction	62
21	Set of Time Delayed Spectra of Emissions from the $O(^1D) + HCl$ Reaction	74
22	Sorting Process Used to Separate Time Delayed Interferograms	75
23	Top View of Reaction Chamber	84
24	Side View of Interior of Reaction Chamber	85
25	Angular Momentum Conservation Effects in: (a) the $O(^1D) + H_2$ Reaction and (b) the $O(^1D) + HCl$ Reaction	94
26	Comparison of the Earliest Spectra taken with the Nicolet and 11/83 Computers	101
27	Time Dependent Vibrational Distribution of OH produced in the $O(^1D) + HCl$ Reaction	102
28	Samples of Time Delayed Spectra for the $O(^1D) + HCl$ Reaction	107
29	Time Dependent Vibrational Distribution of HCl produced in the $O(^1D) + HCl$ Reaction	110
30	Correlation Diagram and Primary Vibrational Distributions for the $O(^1D) + HCl$ Reaction	113
31	Illustrative MC and SL1 Mechanisms	123
32	Samples of Time Delayed Spectra for the $O(^1D) + HBr$ Reaction	130
33	Time Dependent Vibrational Distribution of OH produced in the $O(^1D) + HBr$ Reaction	133
34	Correlation Diagram and Initial OH Vibrational Distribution for the $O(^1D) + HBr$ Reaction	134
35	Time Dependent Vibrational Distribution of OH produced in the $O(^1D) + H_2S$ Reaction	144
36	Time Dependent Vibrational Distribution of OH produced in the $O(^1D) + CH_4$ Reaction	155

CHAPTER 1

(1.1) Introduction: Bond Functions, H_2 and H_3

Many calculations of electronic wave functions and energies rely on expansion of the wave function in terms of a finite number of basis functions. Except for trivial cases, the result is an approximation to the correct wave function. The degree of basis set incompleteness depends on the form of the starting functions, their location and their number. The energies obtained at each molecular geometry are upper bounds for the true energy. In accord with this variational principle, the incompleteness, as measured, for example, by the difference between the obtained energy and the exact, Born-Oppenheimer, nonrelativistic energy, is often assumed to be as small as possible when further addition of any basis functions leads to a negligible energy lowering. However, even for diatomics, the traditional method of using nuclear centered Slater type orbitals (STO's) or contracted Gaussian type orbitals (CGTO's) in some configuration interaction (CI) method often requires prohibitively large basis sets, and for relatively incomplete bases results in molecular descriptions which are much less complete than those of the atomic limit.

The practice of changing the basis set to suit the molecular wave function, possibly at the expense of worsening the description of the atomic limit, is already standard practice^{1, 2, 3}. The optimized exponents for atomic calculations are usually increased by a multiplicative scale factor in order to better describe the molecular wave function. However, even with scaled basis sets, experience with calculations of diatomic potentials has shown that the molecular description is still more incomplete than the atomic description. Thus calculated well depths for diatomics will typically be too small.

One method to improve this situation would be simply to add many further polarization functions (functions with higher angular momentum than necessarily required), which are not involved in the atomic description but which afford a substantially improved^{4, 5} description of the polarization (distortion) of the atom within the molecular environment. Eventually, with enough core functions and polarization functions one might hope to approach the CI limit for both atomic and molecular geometries; however, this requires very large computations.

Another method to achieve a more balanced description is to use functions centered away from the nuclei to enhance the molecular description while not improving the atomic limit at all. Typically this involves the placement of "bond functions" along the bond axis. These functions will be understood to be located at the bond midpoint for the calculations of this work, although this is not a requirement: bond functions may be placed at fixed distances from nuclei, the bond functions may divide the bond axis into three equal portions, or two bond functions may be outside the internuclear region, bracketing the two nuclei. One analysis by Burton⁶ involved the continuous movement of a probe function throughout the length of the bond as a probe of basis set deficiencies.

In fact, bond functions are only a particular way of representing polarization occurring during the formation of the molecule. Whitten's early Gaussian lobe functions⁷ involved simulating higher angular momentum functions by placing *s* orbitals at points in space determined by the symmetry of the orbital to be described. In this light, an *s* orbital at the H₂ bond midpoint may be considered to be partially simulating nuclear-centered *p* orbitals on each hydrogen⁸. Comparison of bond functions with nuclear-centered polarization functions in calculations of energies of methane showed that the effect of 8 bond functions was not improved upon by fewer than 18 conventional polarization functions⁹. This computational advantage of bond functions over conventional polarization functions has been shown to diminish as one increases the basis

set size⁸. However, the use of bond functions with basis sets of moderate size has proven to give excellent results for the first¹⁰ and second row hydrides¹¹, as well as for the particularly intransigent N_2 molecule^{12,13,14}. The usefulness of bond functions in calculations of excited states of diatomics (N_2) has more recently been investigated¹⁵. Bond functions have also been used to construct potential energy surfaces (p.e.s.'s) for the $F(^2P) + H_2$, $O(^1D) + H_2$ and $O(^3P) + H_2$ reactions^{16,17,18}.

The use of basis sets with bond functions determined by a standard procedure to improve the overall shape of the resulting potentials while still retaining relatively incomplete basis sets was investigated by calculations on H_2 and H_3 in this work¹⁹. The optimum bond function basis set was determined empirically for H_2 and the accuracy of this same basis for calculations of the H_3 surface was a particular concern. With this approach, one hopes that problems too expensive computationally using large nuclear-centered bases may become tractable with little or no sacrifice in the quality of the potential surface. Although for diatomics the use of bond functions has already been shown to give excellent relative energies, potential energy surfaces for triatomics are less well characterized, so a conclusive discussion of the accuracy of triatomic surfaces calculated using bond functions has not been possible. H_2 and H_3 were chosen because they would be easy to calculate, and exact (for H_2) or large (for H_3) calculations were available for comparison.

The potential energy curve for H_2 has been accurately calculated by Kolos and Wolniewicz²⁰ (KW) using the variational method (newer data have been published by Kolos et al.²¹). KW obtained a minimum energy for H_2 of -1.174474 hartrees (1 hartree = 27.2116 eV), corresponding to a dissociation energy of 4.7477 eV. The hydrogen atom energy is -0.5 hartrees, described exactly by a single Slater orbital. In 1973, Liu²² calculated 137 collinear geometries of H_3 using a $4s3p2d$ (4 s -, 3 p - and 2 d -orbitals) basis of STO's on each atom. This work was extended to nonlinear geometries by

Siegbahn and Liu²³ (SL) in 1978 using a $4s3p1d$ basis of CGTO's. Although STO's generally do a better job of describing electronic orbitals, calculations of the multicentered electron repulsion integrals are more difficult: the program of SL only treated linear molecules. For these reasons, most of the larger calculations involve CGTO's. In addition, numerous H_2 curves were calculated by SL with CGTO basis sets ranging in size from $4s2p$ to $4s3p1d$. In 1984, the barrier height for the $H + H_2$ reaction was redetermined by Liu²⁴ using $4s2p2d1f$ and $5s3p3d2f$ STO basis sets. A rigorous upper bound for the energy barrier of 0.428 eV resulted from using KW's exact H_2 energy: using the largest basis set the barrier was 0.419 eV and using reasonable estimates of the unrecovered correlation energy, a barrier height of 0.416 ± 0.003 eV was estimated. These values were confirmed by quantum Monte Carlo calculations by Ceperley and Alder²⁵, who obtained a statistical estimate of the energy barrier of 0.418 ± 0.003 eV. An analytical fit to Liu's collinear data, SL's nonlinear data, and KW's H_2 potential was derived by Truhlar and Horowitz²⁶ (TH). The accuracy of this SLTH surface was later reexamined by Blomberg and Liu²⁷, whose further CI calculations confirmed that the SLTH surface was sufficiently accurate to describe the $H/D + H_2(v=1)$ reactions.

(1.2) Method of Calculation

All CI calculations were performed using the MRD-CI (multireference, single and double excitation configuration interaction) program developed by Buenker and Peyerimhoff²⁸. Ground state energies, taking into account singly and doubly excited electronic configurations arising from a reference set of electronic configurations, called "mains", were calculated for H_2 and H_3 . Additional mains were added when their squared CI coefficient was over .005. This empirical procedure ensured that energy

continuity would be maintained when switching to different choices of basis²⁹. Since the systems studied involved at most three electrons, no correction was required for the effect of neglected quadruple excitations. To keep the size of the CI matrices under ~3000 configurations, some H₃ calculations for the largest basis sets at geometries requiring four or more basis used an extrapolation procedure. This extrapolation relied on the convergence of the estimated CI energy, E-CI, with respect to an energy threshold dictating which electronic configurations to include in the CI matrix. Only singly and doubly excited configurations contributing more energy lowering than the selection threshold, when added individually in smaller CI calculations, were included at each threshold energy. When extrapolation was employed, errors of less than 0.03 mhartrees were estimated to have resulted from the 1 mhartree configuration selection threshold which was used¹⁹.

The basis sets used involved CGTO's as radial functions, multiplied by spherical harmonics. A basis set involving one function for each occupied orbital is called a "single zeta" basis set; one involving two functions for each occupied orbital is called "double zeta" (DZ) and three functions per occupied orbital indicates a triple zeta (TZ) basis set. Scaled bases are denoted by an asterisk (e.g., DZ*), and for H the scale factor of 1.2², as determined by Dunning³⁰, was used. The letter 'P' in the basis set denotes additional polarization functions (e.g. 'DZ* + P @ 1.00' to indicate the exponent, or simply 'DZ*P'). For H, these would be three orthogonal *p* orbitals. Bond functions were typically single *s* orbitals ('bf(*s*)'), or an *s* and three *p* orbitals ('bf(*sp*)') with *s* and *p* orbitals having the same exponent (e.g. 'bf(*sp*) @ 1.0'). Polarization and bond function exponents described as optimized were arrived at by optimizing the energy of H₂ at a bond distance of 1.4 bohrs (1 bohr = 0.529177 angstroms) to yield the lowest E-CI energy. The nuclear basis sets and polarization function exponents, to which bond

functions were added, employed standard exponents and contractions obtained from the literature¹⁹.

(1.3) Results and Discussion: H_2

It was a general feature of the exponent optimizations that higher values for the coefficients in the exponents of the basis set functions were biased towards improving the short range molecular description. A preliminary set of calculations presented in table I demonstrates this observation, and it was a general feature which may be noted subsequently in comparisons between the various optimized bases. The best exponents in the table were 0.5, 0.35 and 0.30 for $R_{HH} = 1.0, 2.0$ and 3.0 bohrs respectively; the energetically optimum exponents decreased as the internuclear distance was increased. As may be noted in the table for the 3.0 bohr internuclear distance, the coefficients being optimized should span a large range in order not to converge on a local minimum such as existed here for an exponent around 0.1 .

The behavior of the basis set incompleteness was first investigated for H_2 with some twenty different basis sets. H_2 potentials were calculated for 10-13 points between $R_{HH} = 0.8$ and 5.0 bohrs. Figures 1-6 present plots of the incompleteness, calculated as the difference from the exact potential for H_2 calculated by KW. For comparison, all the figures also display the incompleteness of Liu's $4s3p2d$ basis set²², which is the large basis to which later H_3 calculations will be compared. The incompleteness of Liu's large basis reference calculation for H_2 was zero for the separated atoms and rose almost monotonically as the hydrogens approached one another, reaching a maximum of ~ 0.91 mhartrees (0.025 eV) at $R_{HH} = 0.8$ bohrs. The bond function basis sets did not improve the atomic limit and the bond function exponent values were determined at least within ± 0.05 bohr⁻² to provide a maximal energy lowering at $R_{HH} = 1.4$ bohrs. Thus the bond

Table I: H_2 CI energies calculated using the $DZ^*P + bf(sp)$ basis as a function of internuclear distance and exponent coefficient.

bond function coefficient	E-CI at 1.0 bohr (hartrees)	E-CI at 2.0 bohrs (hartrees)	E-CI at 3.0 bohrs (hartrees)
0.05			-1.05013
0.1	-1.11580	-1.13057	-1.05026
0.2	-1.11681	-1.13172	-1.05021
0.25			-1.05081
0.3	-1.11760	-1.13268	-1.05096
0.35	-1.11781	-1.13275	-1.05088
0.4	-1.11795	-1.13267	-1.05066
0.5	-1.11810	-1.13220	-1.05009
0.6	-1.11806		
0.85	-1.11643	-1.12989	-1.04834

LEGEND

◦	DZ*
•	DZ* + P @ 1.00
◦	DZ*P + bf(s) @ 0.47
◦	DZ*P + bf(sp) @ 0.35
•	DZ*P+2bf(sp)@ 0.35 & 1.0
	Liu 4s3p2d STO

Figure 1: Basis set incompleteness for H₂ as a function of internuclear distance for variations of the DZ* and DZ*P nuclear basis sets. The calculation of the incompleteness assumes the H₂ potential given by Kolos and Wolniewicz (reference 20) as a standard. In each of figures 1-6, the incompleteness at the atomic limit is shown as a dashed line between 5 and 6 bohr and the incompleteness of Liu's 4s3p2d STO basis set is also presented for comparison.

LEGEND

◦	TZ + P @ 0.75
△	TZP + bf(s) @ 2.20
◇	TZP + bf(sp) @ 0.33
<hr/>	
	Liu 4s3p2d STO

Figure 2: Basis set incompleteness for H_2 as a function of internuclear distance for variations of the TZP nuclear basis. Note the change in scale from figure 1.

LEGEND

- TZ + PP @ 1.00 & 0.30
- TZPP + bf(s) @ 2.60
- TZPP + bf(sp) @ 1.05
- Liu 4s3p2d STO

Figure 3: Basis set incompleteness for H₂ as a function of internuclear distance for variations of the TZPP nuclear basis.

LEGEND

- TZ* + P @ 0.75
- △ TZ*P + bf(s) @ 1.90
- TZ*P + bf(sp) @ 1.75
- TZ*P + 2bf(sp) @ 1.55 & 0.32
- Liu 4s3p2d STO

Figure 4: Basis set incompleteness for H₂ as a function of internuclear distance for variations of the TZ*P nuclear basis.

LEGEND	
◦	TZ* + PP @ 1.00 & 0.30
△	TZ*PP + bf(s) @ 1.70
•	TZ*PP + bf(sp) @ 1.30
◦	TZ*PP + 2bf(sp) @ 2.20 & 0.80
---	Liu 4s3p2d STO

Figure 5: Basis set incompleteness for H₂ as a function of internuclear distance for variations of the TZ*PP nuclear basis.

H₂: Energy above KW

13

LEGEND

- TZ*PP + 2bf(sp) @ 2.20 & 0.80
- △ TZ*PP + bf(spd) @ 1.10
- TZ*PP(0.37,2.25)+bf(spd)@1.10
- TZ*PP(0.32,1.65)+2bf(sp)(0.80,2.25)
- Liu 4s3p2d STO

Figure 6: Basis set incompleteness for H₂ as a function of internuclear distance for further variations of the TZ*PP nuclear basis. Note the change in scale from figure 5.

function basis sets commonly display a local minimum in incompleteness around $R_{HH} = 1.4$ bohrs. Since many optimized bases were required, the raw data will not be presented.

The most crude basis set used was the scaled double zeta (DZ^*) basis (see figure 1). The $H + H$ atomic limit was 5.73 mhartrees above the exact value and the incompleteness increased monotonically as the internuclear distance was decreased. At the potential minimum for H_2 , which will be understood to be given by the calculation at $R_{HH} = 1.4$ bohrs in the ensuing presentation, the incompleteness was over 22 mhartrees. The addition of a polarization function (a p orbital with optimized exponent 1.0) was able to decrease the incompleteness at the 1.4 bohr distance to 8.77 mhartrees. Note that since polarization functions do not have the correct symmetry to mix with atomic s -orbitals, the atomic energies of the DZ^* and DZ^*P basis sets were the same. With the further addition of an optimized s bond function ($DZ^*P + bf(s) @ 0.47$) the improvement at 1.4 bohrs was slight. Most improvement occurred for distances $R_{HH} < 1.4$ bohrs. Increasing the basis set to $DZ^*P + bf(sp) @ 0.35$ yielded much lower energies, especially for R_{HH} between 1.4 and 3 bohrs. Since the incompleteness at both 1.4 bohrs and the atomic limit was roughly the same for this basis, the dissociation energy, D_e , for this basis was reasonable, and since the incompleteness was now uniform to within 3 mhartrees, the relative energies of the H_2 potential were correct to within 3 mhartrees at all values of $R_{HH} \geq 0.8$ bohrs. The largest incompleteness occurs at short internuclear distances: the incompleteness varies by 1.9 mhartrees for $R_{HH} \geq 1.0$ bohr. Since for this basis the incompleteness of 5 mhartrees was much larger than the maximum relative error, 3 mhartrees, it was judged that any further attempts to improve the parallelism of the H_2 curve by adding more than one set of polarization and bond functions to the DZ^* basis would not be meaningful. Indeed, the addition of a second (nonoptimized) sp bond function with exponent 1.0 showed little improvement and yielded a dissociation energy of 4.7569 eV. This actually provided a *better* description of the molecule than the atom,

so D_e was thus overestimated. The $DZ^*P + bf(sp) @ 0.35$ basis set exhibited approximate parallelism to the correct curve: it is called a "balanced" basis set, and will subsequently be denoted by "BF1".

The unscaled TZP basis, shown in figure 2, had an incompleteness at the atomic limit of only 0.38 mhartrees, which made this basis set difficult to balance. The addition of an optimized s bond function with exponent 2.2 showed some improvement for $R_{HH} < \sim 2$ bohrs. Greater improvement was noted for the $TZP + bf(sp) @ 0.33$ basis for $R_{HH} \geq 1$ bohr, but the description of the molecular region remained poor relative to the atomic limit. There was still a variation of ~ 7 mhartrees in the incompleteness over the range $R_{HH} \geq 1$ bohr. The tendency for small exponents to improve regions of large R_{HH} was especially evident here.

Starting with a TZPP basis set (figure 3), with the same atomic incompleteness, and adding an optimized s or sp bond function also yielded improvements. The variation in the basis set incompleteness changed from ~ 7 to ~ 5 mhartrees over the range of R_{HH} as the bond functions were added to the basis, and excluding consideration of $R_{HH} < 1.4$ bohrs the incompleteness improved from ~ 4 to ~ 3 mhartrees.

A more significant improvement of the TZP basis was, however, to scale the exponents of this basis set (see figure 4). The incompleteness at the atomic limit was increased from 0.38 to 1.71 mhartrees: the description of the short range potential was bettered at the expense of the description of the long range potential, this being an important step towards a balanced basis. The net effect was to improve the parallelism of the resulting potential from ~ 9 mhartrees (for TZP) to ~ 6 mhartrees (for TZ^*P) over the entire range of R_{HH} considered, with no increase in basis set size. Progression to the optimized $TZ^*P + bf(s) @ 1.9$ and $TZ^*P + bf(sp) @ 1.75$ basis sets improved mostly the inner wall of the potential. A dramatic improvement was shown when two optimized sp bond functions, with exponents 1.55 and 0.32, were used. The incompleteness for R_{HH}

≥ 1.2 bohrs for the $\text{TZ}^*\text{P} + 2\text{bf}(sp)$ @ 1.55 & 0.32 basis varied by 1.3 mhartrees and, including $R_{\text{HH}} \geq 0.8$ bohrs, the incompleteness still varied by only 2.8 mhartrees.

By this point the number of bond functions exceeded the number of polarization functions. Rather than continue in this vein, a second set of nuclear-centered polarization functions was added. The TZ^*PP basis (see figure 5) had only two fewer functions than $\text{TZ}^*\text{P} + 2\text{bf}(sp)$, but showed a much worse (about twice as large) variation in incompleteness of 2.4 mhartrees over the range $R_{\text{HH}} \geq 1.2$ bohrs. This was slowly improved as optimized bond functions were added. A reasonably balanced description of H_2 was arrived at with the $\text{TZ}^*\text{PP} + 2\text{bf}(sp)$ @ 0.8 & 2.2 basis set: the incompleteness varied by 1.1 mhartrees over the range $R_{\text{HH}} \geq 1$ bohr, with a maximum at $R_{\text{HH}} = 3$ bohrs. The incompleteness at the optimization geometry was within 0.38 mhartrees (0.01 eV) of the incompleteness at the atomic limit. This basis set will be referred to as "BF2".

The dissociation energy and the atomic energy are two convenient measures of basis set quality. D_e , taken as the energy at 1.40 bohrs minus twice the atomic energy, is presented in table II for all the H_2 basis sets considered, and for some basis sets taken from the literature. The dissociation energy of the hydrogen molecule is 4.7477 eV. The TZP basis yielded a better D_e (4.5911 eV) and atomic energy than the DZP basis ($D_e = 4.4665$ eV); however, a worse D_e was yielded by the TZ^*P basis (4.6282 eV) when compared to the DZ^*P basis (4.6377 eV). The smaller D_e in the latter comparison occurred because the improvement in atomic description was larger than the improvement in the molecular description for this particular increase to a larger set of nuclear s orbitals. For both the TZP and TZ^*P basis sets, the addition of a second set of nuclear polarization functions afforded a 0.06 eV increase in D_e while not affecting the atomic energy. Addition of bond functions yielded still better D_e 's.

Dissociation energies of 4.7341 and 4.7368 eV were yielded by the BF1 and BF2 basis sets respectively. Three basis sets similar to BF2 in quality are also presented in

Table II: Parameters of different bases for H₂.

Nuclear Orbitals	Bond Functions	Number of CGTO's	Atomic energy (hartree)	Dissociation energy (eV)
DZP	...	10	-.49928	4.4665
DZ*	...	4	-.49763	4.2512
DZ*P	...	10	-.49763	4.6377
DZ*P	<i>s</i> @ 0.47	11	-.49763	4.6450
DZ*P	<i>sp</i> @ 0.35	14	-.49763	4.7341
TZP	...	12	-.49981	4.5911
TZP	<i>s</i> @ 2.20	13	-.49981	4.6145
TZP	<i>sp</i> @ 0.33	16	-.49981	4.6319
TZPP	...	18	-.49981	4.6523
TZPP	<i>s</i> @ 1.70	19	-.49981	4.6633
TZPP	<i>sp</i> @ 1.30	22	-.49981	4.6841
TZ*P	...	12	-.49915	4.6282
TZ*P	<i>s</i> @ 1.40	13	-.49915	4.6583
TZ*P	<i>sp</i> @ 1.75	16	-.49915	4.6744
TZ*P	<i>2sp</i> @ 1.55, 0.32	20	-.49915	4.7224
TZ*PP	...	18	-.49915	4.6896
TZ*PP	<i>s</i> @ 1.70	19	-.49915	4.7058
TZ*PP	<i>sp</i> @ 1.30	22	-.49915	4.7256
TZ*PP	<i>2sp</i> @ 2.20, 0.80	26	-.49915	4.7368
TZ*PP	<i>spd</i> @ 1.10	28	-.49915	4.7427
TZ*PP ^a	<i>spd</i> @ 1.10	28	-.49915	4.7490
TZ*PP ^b	<i>2sp</i> @ 2.25, 0.80	26	-.49915	4.7404
3s3p1d ^c	...	34	-.49981	4.688
4s3p1d ^d	...	36	-.499998	4.716
4s3p2d ^e	...	46	-.50000	4.7268
5s3p3d2f ^f	...	86	-.50000	4.7387
exact ^g	...	...	-.50000	4.7477

^aPolarization exponents reoptimized to give 2.25, 0.37^bPolarization exponents reoptimized to give 1.65, 0.32^cM. J. Frisch, J. S. Binkley and H. F. Schaefer III, *J. Chem. Phys.* **81**, 1882 (1984)^dP. Siegbahn and B. Liu, *J. Chem. Phys.* **68**, 2457 (1978)^eB. Liu, *J. Chem. Phys.* **58**, 1925 (1973)^fB. Liu, *J. Chem. Phys.* **80**, 581 (1984)^gW. Kolos and L. Wolniewicz, *J. Chem. Phys.* **43**, 2429 (1965)

figure 6. The first involved using a single set of *spd* bond functions in place of two sets of *sp* bond functions and gave a D_e of 4.7427 eV. The second involved reoptimization of the polarization function exponents of the first basis set. The third basis set entailed reoptimizing the polarization function exponents of the BF2 basis followed by a slight adjustment in the exponents of the two bond functions and yielded a D_e of 4.7404 eV. The incompleteness of these basis sets over an extended range of R_{HH} was very similar to the BF2 basis. Since part of the original motivation for this work was to prescribe fairly standard methods of developing basis sets, none of these three basis sets was used in subsequent H_3 calculations, in spite of the improved D_e 's which they afforded, because of a desire to respect the following guidelines: the highest spherical harmonics present should not be located in bond functions, and the atomic basis set should be obtainable from the literature with little further reoptimization for any particular molecule.

Also of interest in table II is the difference in size between the $TZ^*PP H_2$ bases and the large bases reported in the literature. Some of the bond function basis sets achieved better D_e 's than nuclear centered bases which were over three times as large. Liu's $4s3p2d$ basis, the incompleteness of which was displayed in figures 1-6, contained 46 STO's, yet its potential curve was parallel to KW to within 0.9 mhartrees. With the BF2 basis set, parallelism to within 1.1 mhartrees was achieved with but 26 CGTO's. Additionally, the dissociation energy was better described with the BF2 basis. Because the incompleteness curves for the bond function basis sets tended to show local minima around $R_{HH} = 1.4$ bohrs and local maxima at $R_{HH} \sim 3$ bohrs, one may expect that force constants displayed by such bases would be higher than those calculated using a large, nuclear-centered basis whose incompleteness is flatter around the equilibrium geometry. For example, the variation in incompleteness for the restricted range $1 \leq R_{HH} \leq 3$ bohrs was 0.73 mhartrees for the BF2 basis, but only 0.19 mhartrees for Liu's $4s3p2d$ basis.

(1.4) H_3 : the Rotated Morse Curve Method

The collinear H_3 surfaces were constructed using the rotated Morse curve, cubic spline (RMCS) technique³¹. Briefly, this involves taking a swing point far out on the 45° ray (for these surfaces at $R_{HH} = 9.45$ bohr), fitting points calculated along rays through this point to 5-parameter generalized Morse functions (GMF5's), and then splining the GMF parameters as a function of the swing angle. Since the surface is symmetric, only points on rays for swing angles up to 45° were calculated. The GMF5 function had the form

$$V(l) = D[1 - \exp(\beta(l - l_e))]^2 - D,$$

where l (the 'swing distance') is the distance from the swing point along the swing ray, l_e is the distance from the swing point to the potential minimum on that ray, D is the well depth, and

$$\beta = \beta_0[1 + \lambda_1(l - l_e) + \lambda_2(l - l_e)^2].$$

The five parameters $D(\theta)$, $l_e(\theta)$, $\beta_0(\theta)$, $\lambda_1(\theta)$ and $\lambda_2(\theta)$ are functions of the swing angle, θ . The swing angles chosen were 0, 15, 25, 33, 37, 39, 41, 43 and 45° , with the convention that 0° correspond to the $H + H_2$ limit. The points used for the GMF5 fits were concentrated around the potential well, and for the final surface the inner- and outer-most points calculated were not used. This resulted in 8 or 9 points being used in the GMF5 fits, with most points lower than 1 eV below the dissociation limit. RMS deviations of the GMF5 fits were typically less than 0.01 eV. Along the 45° ray, points were calculated at the same geometries reported by Liu.

(1.5) Results and Discussion: H_3

The basis sets used for the H_3 RMCS surfaces were: DZ^* , DZ^*P , BF1 ($DZ^*P + \text{bf}(sp)$), TZ^*PP and BF2 ($TZ^*PP + 2\text{bf}(\omega p)$). The Morse parameters defining the H_3

surfaces are listed in table III and the splined fits to these data are plotted in figures 7-11. The values of the λ_1 and λ_2 parameters typically showed much variation, especially around the 45° swing angle. These less critical fitting parameters were subject to numerical variations arising from the particular geometries used to fit each ray, being especially dependent on fitting the more extended geometries. Contour plots of the resulting surfaces and the SLTH surface are shown in figures 12-14 and appear to be quite smooth. The minimum energy path (MEP) is shown in all surface plots as a dashed line and the contour interval in these plots is 0.5 eV. The H_3 surface is repulsive, with a saddle point on the 45° ray at R_{HH} near 1.757 bohrs. The only evidence of the ambiguity in the least well-defined Morse parameters was in difference plots (figures 15-19) comparing the RMCS surfaces with the more smooth SLTH function. The 45° and 43° rays are evident in these difference plots at extended H_3 geometries. Since triatomic configurations required more polarization of the atomic orbitals than diatomic ones and diatomic geometries involve more polarization than the dissociated atoms, the energy barrier, E_b , with respect to the $H + H_2$ limit was overestimated by basis sets which favored the atomic description. The size of each basis and the energies of H , H_2 ($R_{HH} = 1.4$ bohrs), and the transition state of H_3 ($R_{HH} = 1.757$ bohrs) are listed in table IV for reference.

The RMCS H_3 surfaces were compared at all 137 of Liu's geometries²² to Liu's CI data. Liu's data sample geometries concentrated along the MEP. Liu's energies, except at some geometries on the 45° swing ray, were in the lower half of the energy range spanned by the entire H_3 surface. These comparisons, where the zero of energy was set at the dissociation limit, may be found in table V, along with comparisons to Liu's 15 points for linear equidistant H_3 . This subset of geometries on the 45° swing ray exhibited slightly larger deviations from Liu's surface and was also the least well fitted by the GMF functions used in constructing the RMCS surface. Liu's collinear data,

Table III: Rotated Morse Curve Fits for
collinear H_3 surfaces

Swing Angle, θ (degrees)	$D(\theta)$ (eV)	$\beta_0(\theta)$ (bohr ⁻¹)	$I_c(\theta)$ (bohr)	$\lambda_1(\theta)$ (bohr ⁻¹)	$\lambda_2(\theta)$ (bohr ⁻²)
DZ*					
0.0	4.252668	1.084359	8.039617	0.061359	0.051828
15.0	4.255882	1.048194	8.321968	0.053676	0.045032
25.0	4.257159	0.983798	8.869391	0.050534	0.039457
33.0	4.230679	0.909517	9.579791	0.047266	0.034461
37.0	4.145121	0.861834	10.040764	0.040142	0.030600
39.0	4.045915	0.834281	10.290992	0.034141	0.028477
41.0	3.891533	0.802280	10.539374	0.021878	0.025037
43.0	3.715932	0.769624	10.751900	0.003613	0.020418
45.0	3.631026	0.753962	10.844014	-.014622	0.013589
DZ*P					
0.0	4.639653	1.078053	8.050484	0.051029	0.051994
15.0	4.643786	1.042061	8.337226	0.041672	0.044180
25.0	4.645722	0.978151	8.885648	0.039260	0.038608
33.0	4.622196	0.904381	9.597737	0.037313	0.033943
37.0	4.542207	0.856901	10.061218	0.030292	0.029980
39.0	4.451611	0.830193	10.314625	0.024437	0.027655
41.0	4.315102	0.799601	10.568939	0.011517	0.023550
43.0	4.167733	0.769155	10.790625	-.006455	0.018513
45.0	4.097257	0.753381	10.887457	-.026341	0.011121
TZ*PP					
0.0	4.691710	1.047310	8.048230	0.060633	0.054008
15.0	4.696274	1.012340	8.330459	0.051364	0.046243
25.0	4.698444	0.950117	8.878210	0.048049	0.040272
33.0	4.680257	0.877947	9.590066	0.045927	0.035568
37.0	4.614939	0.831380	10.053717	0.038869	0.031550
39.0	4.538877	0.804638	10.558707	0.032823	0.025468
41.0	4.421740	0.773037	10.777021	0.019525	0.020325
43.0	4.296661	0.740959	10.777021	0.000310	0.020325
45.0	4.240028	0.721203	10.872924	-.013179	0.019232

**Table III: Rotated Morse Curve Fits for
collinear H₃ surfaces (continued)**

Swing Angle, θ (degrees)	$D(\theta)$ (eV)	$\beta_0(\theta)$ (bohr ⁻¹)	$I_e(\theta)$ (bohr)	$\lambda_1(\theta)$ (bohr ⁻¹)	$\lambda_2(\theta)$ (bohr ⁻²)
<i>BF1 (DZ*P + bf(sp) @ 0.35)</i>					
0.0	4.735676	1.046620	8.047468	0.060040	0.054494
15.0	4.743825	1.011319	8.329618	0.050564	0.046288
25.0	4.749742	0.949051	8.877447	0.047647	0.040453
33.0	4.736979	0.876044	9.587493	0.042562	0.034459
37.0	4.675943	0.829279	10.051968	0.037594	0.031243
39.0	4.601133	0.802669	10.304657	0.031524	0.028816
41.0	4.484141	0.771645	10.556589	0.018203	0.024706
43.0	4.356113	0.740125	10.774157	0.000087	0.019966
45.0	4.299664	0.720812	10.870218	-0.013787	0.018312
<i>BF2 (TZ*PP + 2bf(sp) @ 0.80 & 2.20)</i>					
0.0	4.739520	1.040469	8.047814	0.051321	0.048533
15.0	4.744139	1.007794	8.332400	0.054349	0.047063
25.0	4.746778	0.945737	8.880354	0.051217	0.041135
33.0	4.730379	0.873924	9.592298	0.048509	0.036082
37.0	4.667292	0.827039	10.056204	0.041398	0.032151
39.0	4.594038	0.800283	10.309327	0.035161	0.029794
41.0	4.480593	0.768497	10.561797	0.022081	0.026050
43.0	4.357862	0.735974	10.778497	0.001059	0.020374
45.0	4.305124	0.715242	10.876050	-0.010860	0.020140

Figure 7: Plots of the GMF5 parameter D_e as a function of the swing angle, θ .

Figure 8: Plots of the GMF5 parameter l_e as a function of the swing angle, θ .

Figure 9: Plots of the GMF5 parameter β_0 as a function of the swing angle, θ .

Figure 10: Plots of the GMF5 parameter λ_1 as a function of the swing angle, θ .

Figure 11: Plots of the GMF5 parameter λ_2 as a function of the swing angle, θ .

Figure 12: Contour plots of H_3 potential energy surfaces calculated with DZ^* and ($DZ^* + P @ 1.00$) basis sets. The contour interval is 0.5 eV and the zero of energy is taken to be at the dissociation limit.

Figure 13: Contour plots (as in figure 12) of the H_3 potential energy surfaces calculated with (DZ*P + bf(sp) @ 0.35) ("BF1") and (TZ* + PP @ 1.00 & 0.30) basis sets.

H₃: SLTH surface

Figure 14: Contour plots (as in figure 12) of the H₃ potential energy surfaces calculated with (TZ*PP + 2bf(sp) @ 2.20 & 0.80) ("BF2") basis set and the analytical function of SLTH (see reference 26).

Table IV: Characteristics of basis sets used in H_3 calculations (energies in hartrees)

Basis Set	E(H)	E(H ₂) (R _{HH} = 1.4 bohrs)	E(H+H ₂)	E(H ₃) (R _{HH} =1.757 bohrs)	Number of functions
DZ*	-.497634	-1.151489	-1.649123	-1.626208	6
DZ*P	-.497634	-1.165700	-1.663334	-1.643377	15
BF1	-.497634	-1.169240	-1.666874	-1.650876	23
TZ*PP	-.499147	-1.170634	-1.669781	-1.653254	27
BF2	-.499147	-1.172372	-1.671519	-1.655616	43
4s3p2d ^a	-.500000	-1.17370	-1.67370	-1.658083 ^b	69
4s3p1d ^c	-.499998	-1.173313	-1.673311	-1.65753	54
5s3p3d2f ^d	-.500000	-1.174142	-1.674142	-1.658755	129

^aB. Liu, *J. Chem. Phys.* **58**, 1925 (1973)

^bCalculation done at R_{HH} = 1.75 bohrs

^cP. Siegbahn and B. Liu, *J. Chem. Phys.* **68**, 2457 (1978)

^dB. Liu, *J. Chem. Phys.* **80**, 581 (1984)

Table V: Average difference in energy between RMCS H_3 surfaces and Liu's original data points (eV)

Basis Set	Points on 45 degree ray	All Points
DZ*	0.57 ± 0.22	0.56 ± 0.11
DZ*P	0.214 ± 0.046	0.174 ± 0.045
BF1	0.026 ± 0.030	0.003 ± 0.022
TZ*PP	0.068 ± 0.013	0.055 ± 0.015
BF2	0.009 ± 0.021	-0.002 ± 0.011
SLTH ^a	0.001 ± 0.003	-0.001 ± 0.004

^aD. G. Truhlar and C. J. Horowitz, *J. Chem. Phys.* **68**, 2466 (1978)

combined with the exact H_2 limit of KW and the noncollinear data of Siegbahn and Liu²³, was represented analytically by the SLTH fitting function, which had an average difference from Liu's collinear data of -0.001 ± 0.003 eV along the 45° ray, an overall average difference of -0.001 ± 0.004 and a maximum deviation of 0.01 eV. In comparison, the basis sets BF1 and BF2 had overall average differences of 0.003 ± 0.022 and -0.002 ± 0.011 eV respectively. The low average difference means that the large scale energetics of the two RMCS surfaces were quite similar to Liu's data, while the larger standard deviations implied the existence of both positive and negative local variations at the geometries sampled by Liu's data. Thus a measure of parallelism along the reaction path is proffered by the standard deviation of the energy differences. In progressing from the DZ^* nuclear-centered basis, through the DZ^*P basis, to the BF1 basis, dramatic improvements in both the overall energetics and the parallelism along the MEP were noted (see table V). In contrast, the addition of bond functions to the TZ^*PP basis improved the overall energetics greatly, but increased the parallelism along the MEP to a lesser extent.

Another method of judging the RMCS surfaces involves the transition state properties presented in table VI. This table presents the saddle point geometry, force constants and E_b , the barrier height. The symmetric stretch, symmetric bend and antisymmetric stretch are described by force constants A_{11} , A_{22} and A_{33} respectively. The transition state properties were determined by a least squares fitting technique as described by Liu²²; for this a few additional calculations were required. The geometries important for the calculation of A_{33} were at the swing distance of the saddle point (which minimized the potential energy of a preliminary fit along the symmetric stretch), but at swing angles $\theta = 44.8$ and 44.6° . The symmetric bend was described, as in reference 23, by calculations at bond angles of 180 , 176 and 172° in the lower C_s symmetry. Differences in the force constants signify local deviations from parallelism in

Table VI: Transition state properties

Basis Set	E_b (eV)	R_{HH} (bohr)	A_{11}	A_{22} (hartree bohr ²)	A_{33}
DZ*	0.621	1.779	.342		
DZ*P	0.543	1.751	.335	.026	-.075
BF1	0.436	1.765	.339	.022	-.065
TZ*PP	0.450	1.762	.333	.022	-.064
BF2	0.432	1.761	.328	.022	-.059
4s3p2d ^a	0.425	1.757	.320		-.058
4s3p1d ^b	0.429	1.757		.021	
5s3p3d2f ^c	0.416	1.759			
Monte Carlo ^d	0.418				

^aB. Liu, *J. Chem. Phys.* **58**, 1925 (1973)

^bP. Siegbahn and B. Liu, *J. Chem. Phys.* **68**, 2457 (1978)

^cLiu's best estimate for E_b of 0.416 ± 0.003 eV was based on extrapolations of his largest CI calculations. See reference 24.

^dCeperley and Alder's statistical estimate; ± 0.003 eV. See reference 25.

the transition state region. The force constant most sensitive to these changes in basis set was the antisymmetric stretch. One notes that the TZ*PP basis did better than the "balanced" BF1 basis for both the A_{11} and A_{33} force constants. This effect on force constants, for the symmetric stretch, was an extension of the prediction made in the discussion of the H_2 calculations: evidently, the local behavior of the basis set incompleteness around the $R_{HH} = 1.4$ bohr minimum energy geometry for H_2 had been extended along the MEP throughout the H_3 calculations with the BF1 basis set. This indicates that the orbital distortions are roughly equally well described for H_2 and H_3 by the bond function basis set. The "balanced" BF2 basis, in comparison, was in excellent agreement with force constants derived from Liu and SL's calculations. Not only was the incompleteness of the BF2 basis "balanced" at the equilibrium H_2 geometry, but the variation in incompleteness was much smaller than for the BF1 basis. This important distinction between the quality of the BF1 and BF2 basis sets extended to the triatomic surface calculation as well. Both BF1 and BF2 energy barriers of 0.436 and 0.432 eV respectively showed reasonable agreement with Liu's $4s3p2d$ barrier of 0.425 eV. The best estimate of E_b is 0.418 ± 0.003 eV, obtained by Ceperley and Alder²⁵ using a quantum Monte Carlo method.

The contour maps of the energy differences between the RMCS and SLTH surfaces (figures 15-19) have a contour interval of 0.01 eV and the dissociation limit is again fixed at zero. The MEP of the RMCS surface is shown as a dotted line. The DZ^* surface lay far above the SLTH surface (see figure 15), and got progressively worse as one approached the transition state or repulsive inner walls of the potential. For purposes of comparing directly to Liu's data, $R_{HH} = 1.75$ bohrs will be treated as the H_3 transition state with negligible error. The transition state energy for the DZ^* RMCS H_3 surface lay 0.676 eV above Liu's $4s3p2d$ calculation and, relative to the $H + H_2$ limit, yielded a barrier height of 0.621 eV. The dissociation energy for this basis was incorrect by 10%.

Figure 15: Contour plot of the difference in energy between potential surfaces calculated by using the DZ* basis and by using the analytical potential of SLTH. The contour interval in figures 15-19 is 0.01 eV.

Figure 16: Contour plot (as in figure 15) of the difference in energy between potential surfaces calculated by using the DZ^*P basis and by using the analytical potential of SLTH.

Figure 17: Contour plot (as in figure 15) of the difference in energy between potential surfaces calculated by using the DZ*P + bf(sp) @ 0.35 ("BF1") basis and by using the analytical potential of SLTH.

Figure 18: Contour plot (as in figure 15) of the difference in energy between potential surfaces calculated by using the TZ*PP basis and by using the analytical potential of SLTH.

Figure 19: Contour plot (as in figure 15) of the difference in energy between potential surfaces calculated by using the TZ*PP + 2bf(sp) @ 2.20 & 0.80 ("BF2") basis and by using the analytical potential of SLTH.

and the barrier height was incorrect by 49% — an example of the increased difficulty of describing triatomic surface features rather than a diatomic potential energy curve.

Progressing to the DZ*P basis (figure 16), one found the transition state energy of the RMCS surface 0.206 eV above Liu's value and the barrier height decreased to 0.543 eV. The difference energy plot now displayed a minimum, roughly along the MEP, which extended across the transition region. What in the difference energy plot (figure 1) for H₂ was a poor description around $R_{HH} = 3$ bohrs was evident as a hump on the dissociative side of the MEP for H₃; this hump became more prominent as one approached the 45° ray. Similarly, the rapidly degrading description of the repulsive wall for H₂ was seen to continue for H₃. For this basis, D_e was too small by 2.3% and E_b too large by 30%.

This is to be contrasted with the BF1 basis set which was found to be reasonably "balanced" for H₂, having only a 0.29% error in D_e . The BF1 RMCS surface yielded a transition state energy only 0.003 eV above Liu's. The error in the 0.436 eV energy barrier on the BF1 surface was 4.3%, the addition of a single optimized set of *sp* bond functions having decreased the 30% error in E_b for the DZ*P basis by a factor of seven. This improvement is evident in the difference energy plots for the DZ*P and BF1 bases (figures 16-17), which show the MEP to be flatter and the dissociative side of the MEP to have much sparser contour lines.

Similar comparisons hold for the TZ*PP and BF2 basis sets (figures 18-19). The TZ*PP surface was 0.062 eV above Liu's value while the BF2 surface was only 0.003 eV above. The addition of two optimized *sp* bond functions to the TZ*PP nuclear-centered basis decreased the error in D_e from 1.2% to 0.22%; and the error in E_b from 7.6% to 3.3%. The paucity of contour lines in the TZ*PP difference map indicates the high degree of parallelism between the TZ*PP and SLTH surfaces. The elevation of these contour lines is much reduced in the BF2 difference energy map reflecting the better

global behavior of this basis, although the density of contour lines remains much the same in the MEP region. These features were noted earlier in the direct comparison to Liu's values (table V). The difference energy maps indicate that the most noteworthy local improvement of the surface obtained by using the BF2 basis is on the repulsive side of the MEP, near the 45° ray. Once again it is evident that a basis set of modest size which provided a reasonably balanced description of the diatomic curve also provided excellent results for the triatomic surface. It should be remembered that, unlike comparisons for H_2 , Liu's much larger $4s3p2d$ STO basis itself was deficient in the triatomic interaction region, yielding E_b too large by 1.7%. What is significant is that similar surfaces could be obtained with much smaller basis sets.

The preceding figures and tables have taken the zero of energy to be at the dissociation limit, except for the values quoted for E_b . Limiting one's concern solely to the MEP characteristics, one may wish to compare energies relative to the $H + H_2$ entrance channel. Using this convention, the energies of linear equidistant H_3 are shown in table VII for the CI data points used for the RMCS surfaces, Liu's data, and the SLTH fitting function. Although the parallelism along the MEP of the TZ*PP surface had been seen earlier to be reasonable, the BF2 surface was seen to be closer to Liu's data over the extended range of points presented in table VII.

The question of basis superposition error (BSSE) arises in calculations of this type. BSSE refers to a possible artifact arising when substantially incomplete atomic bases are used and involves the improvement in the purely atomic description caused by the presence of any external orbitals in the molecular environment, irrespective of any molecular effects. The Boys-Bernardi counterpoise procedure³² is often used to estimate the maximum possible value for the BSSE. The procedure involves calculating, for each atom of the molecule and at each molecular geometry, the improvement in atomic energy resulting from the addition of all external orbitals to the atomic basis without adding the

Table VII: CI energies for linear equidistant H_3 . Energy in eV relative to $H + H_2$ in the same basis set

R(bohr)	DZ*	DZ*P	BF1	TZ*PP	BF2	Liu ^a	SLTH ^b
1.1	4.809	4.583	4.553	4.451	4.440	4.383	4.379
1.3	2.246	2.057	1.999	1.981	1.944	1.917	1.921
1.5	1.060	0.913	0.839	0.843	0.816	0.802	0.803
1.6	0.785	0.663	0.575	0.587	0.563	0.552	0.552
1.7	0.650	0.555	0.454	0.466	0.449	0.440	0.440
1.75	0.625	0.543	0.436	0.450	0.432	0.425	0.425
1.757	0.624	0.543	0.435	0.449	0.433		
1.8	0.623	0.554	0.441	0.456	0.439	0.432	0.433
1.9	0.672	0.631	0.507	0.523	0.506	0.502	0.503
2.1	0.924	0.943	0.802	0.817	0.802	0.797	0.799
2.3	1.289	1.370	1.222	1.230	1.218	1.209	1.212
2.5	1.696	1.839	1.689	1.692	1.683	1.670	1.673
2.7	2.104	2.306	2.159	2.157	2.152	2.134	2.136
3.0	2.664	2.931	2.812	2.803	2.804	2.781	2.781
4.0	3.816	4.181	4.186	4.156	4.182	4.147	4.161
5.0	4.155	4.534	4.608	4.570	4.609	4.600	4.610
∞	4.251	4.662	4.734	4.690	4.737	4.727	4.748

^aSee reference 22

^bSee reference 26

Table VIII: BSSE for the BF1 basis set

R_{HH} (bohr)	BF1 - KW ^a Incompleteness (mhartree)	DZ*P - BF1 Improvement (mhartree)	BSSE (mhartree)
0.8	7.28	4.79	0.326
0.9	6.53	3.83	0.344
1.0	5.90	3.31	0.346
1.2	4.92	3.12	0.342
1.3	4.60	3.28	0.350
1.4	4.39	3.54	0.364
1.6	4.28	4.17	0.406
2.0	4.71	5.27	0.504
2.4	5.40	5.66	0.574
3.0	6.18	4.75	0.590
3.5	6.24	3.22	0.544
4.0	5.90	1.85	0.474
5.0	5.11	0.48	0.324
∞	4.74	0.0	0.0

^aSee reference 20

other nuclei themselves. The sum of the individual atomic improvements is then the BSSE estimate for the molecule. For H_2 , this involved calculating the SCF energies of the hydrogen atom in the presence of bond functions and the "ghost" orbitals of the second H atom. Twice the improvement in the H atom energy was then the BSSE for the H_2 molecule. Table VIII presents, as a function of R_{HH} , the incompleteness of the BF1 basis, the improvement resulting from the addition of bond functions to the DZ^*P basis (i.e. the difference between the DZ^*P and BF1 basis sets) and the BSSE of the BF1 basis. The BSSE was always less than 0.6 mhartrees and for $R_{HH} < \sim 3$ bohrs the BSSE was responsible for only $\sim 10\%$ of the improvement caused by the bond functions. Also, the BSSE was also always less than $\sim 10\%$ of the total incompleteness of the BF1 basis. As had been noted in calculations of van der Waal's interactions and as was evident in table VIII, for detailed calculations of long-range potentials the BSSE comprised a larger proportion of the energy lowering; however, the description of the long-range potential was not a vital facet of the present calculations. The effect of bond functions was not an "artificial" result stemming from a fortuitous cancellation of incompleteness by the BSSE. Wright and Kruus¹⁹ presented extended calculations of the BSSE for H_2 using the DZ^*P , BF1, TZ^*PP and BF2 bases. The largest BSSE was displayed by the BF1 basis set. This paper presented a detailed discussion of BSSE and the use of bond functions in an effort to allay suspicions about the validity of the technique of using bond functions. Further discussion of BSSE and the counterpoise correction may be found in reference 19.

(1.6) Conclusions

The investigation of basis set effects on H_2 potential curves showed large benefits were realizable by the simple process of adding bond functions to standard, scaled, small-

or intermediate-sized nuclear basis sets. The number of bond functions, with exponents optimized near the minimum of the potential curve, was increased until the dissociation energy for the molecule was close to the correct value. Two balanced basis sets determined in this fashion were the $DZ^*P + bf(sp)$ and $TZ^*PP + 2bf(sp)$ bases, denoted by BF1 and BF2 respectively. These sets showed good parallelism to the KW reference curve over the entire range of internuclear distances. The BF2 basis achieved parallelism within 1.1 mhartrees for $R_{HH} > \sim 0.9$ bohrs, on par with Liu's larger $4s3p2d$ nuclear-centered basis which had a 0.9 mhartree variation in incompleteness; however, the BF2 basis used only 26 CGTO's, while the $4s3p2d$ basis used 46 CGTO's.

The effect of bond function basis sets balanced for diatomics upon the H_3 surfaces calculated with these balanced bases was investigated. Addition of bond functions to the DZ^*P and TZ^*PP nuclear-centered bases resulted in large improvements over the entire H_3 surface. The energy barrier for the BF2 surface was 0.432 eV, as compared to 0.425 eV for Liu's $4s3p2d$ basis and the best estimate of 0.418 ± 0.003 eV. The BF2 surface was very reliable along the MEP, and the collinear dynamics should be similar to that of the SLTH surface. For H_3 , the BF2 basis involved 43 functions, yet it performed almost as well as the 69 functions of Liu's $4s3p2d$ nuclear-centered basis.

The practical importance of this study involved the possible extension of bond function basis sets balanced for diatomics to more difficult, triatomic systems, such as $O(^3P/{}^1D) + H_2$ and $F(^2P) + H_2$. For the prototypical $H + H_2$ system investigated in this thesis, the percentage errors in D_e for the BF1, BF2, and Liu's $4s3p2d$ bases were 0.29%, 0.22% and 0.44% respectively, while the corresponding errors in E_b were 4.3%, 3.3% and 1.7%. Although the diatomic D_e 's were well described ("by construction") by the balanced bond function bases, the description of the triatomic surface feature, E_b , was less accurate. Calculations with larger basis sets showed less deterioration in quality

when extended to the triatomic system. Basis set superposition error was not an important factor in these calculations.

Regarding computational feasibility, especially of triatomic surfaces involving many more electrons, these results indicate that a bond function approach may well remain a method of choice if extended surface calculations are to be performed. Larger polyatomics contain a larger proportion of possible bond function sites in comparison to the number of nuclear sites. This factor decreases the benefit of bond function bases from the point of view of basis set size. Also, larger polyatomics will be more susceptible to problems with linear dependencies as the number of possibilities for closely spaced bond function sites increases. Thus, it is likely that extension of bond function calculations to larger polyatomics will result in further deficiencies when compared with large basis calculations.

In comparing the energetic improvement of the BF2 basis (26 CGTO's for H_2 ; 43 for H_3) over the BF1 basis (14 CGTO's for H_2 ; 23 for H_3), one already sees evidence of "diminishing returns" with respect to the size of the basis set. For this reason, the addition of large numbers of bond functions onto nuclear-centered bases larger than TZ*PP is unlikely to be very fruitful.

If from the outset one is restricted to calculations of intermediate size, a bond function basis set is to be recommended. In particular, a basis set consisting of TZ*PP nuclear functions with two sets of optimized *sp* bond functions is recommended as a likely candidate for a balanced basis in triatomic calculations. The utility of bond function basis sets of intermediate size in achieving relative energetics similar in quality to calculations done with large, atom-centered basis sets has been demonstrated.

CHAPTER 2

(2.1) Overview of O(¹D) Reactions

The lowest electronically excited state of the oxygen atom, O(¹D), plays an important part in stratospheric chemistry³³. O(¹D) is formed in the stratosphere by the photodissociation of ozone, O₃, in the Hartley band³⁴ in the 220-290 nm spectral region. O(¹D) is metastable, with a radiative lifetime for the magnetic dipole transition at 630 nm to the O(³P) ground state of³⁵ $\tau_{\text{rad}} = 140$ s. This allows considerable opportunity for O(¹D) to be quenched or to react in collisions instead of relaxing radiatively to the ground state. Nearly all the stratospheric O(¹D) is deactivated by collisions with N₂³⁶, O₂³⁷, CO³⁸ or CO₂³⁹ and causes substantial vibrational excitation of these collision partners⁴⁰: the more minor reactions of O(¹D) with H₂O, H₂ and simple hydrocarbons form the primary source of stratospheric OH, while the reaction with N₂O produces NO. NO and OH play important roles in controlling the ozone concentration in the stratosphere. Catalytic destruction cycles of the form

where X = HO, NO, Cl or Br, control the concentration of ozone. OH, besides being directly involved, may also be indirectly involved as an initiator of such catalytic cycles: one of the few sources of free Cl is the reaction of HCl, one of the principal chlorine-containing species in the stratosphere⁴¹, with either OH⁴² or O(¹D)⁴³.

Since the deactivation and reaction rates of O(¹D) are of great importance to kinetic models of the atmosphere, many studies have measured the thermal⁴⁴ or temperature dependent⁴⁵ rate constants and branching ratios for these processes. Since the electronic energy of the O(¹D) atom is released, these reactions tend to be exothermic

and proceed rapidly. The rates of $O(^1D)$ reactions are usually limited by the collision frequency. These "gas kinetic" rate constants (corresponding to typical hard-sphere collision frequencies) are typically on the order of $10^{-10} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$. A series of detailed reviews of measurements of atmospheric rate constants has appeared between 1980 and 1984^{46,47,48}.

Furthermore, during the past decade many measurements of the internal state distributions of the OH product of $O(^1D)$ reactions with hydrogen containing species have been undertaken to understand the dynamics of these reactions. Electronic excitation of the oxygen atom can result in significant changes in reaction rates. To a lesser extent, a knowledge of the extent of internal excitation in molecules is important for simulations of stratospheric chemistry for a similar reason: most usually, the reaction rate is increased by internal excitation of the reagents. Depending on the form of the internal energy and the specific reaction, the reactivity may be enhanced by several orders of magnitude. This presents a more practical reason to study the internal state distributions of products of reactions involved in stratospheric chemistry.

In this chapter, we will present a description of the general features of

reactions and introduce several techniques which have been used to study these reactions. Many of the features of such reactions are displayed by the prototype $O(^1D) + H_2$ reaction, which has received much experimental and theoretical attention and has been recently reviewed by Sloan⁴⁹. Since the $O(^1D)$ - $O(^3P)$ separation of the oxygen atom is 189 kJ/mol, such reactions are typically quite exothermic, being able to populate several OH vibrational levels and typically yielding highly excited rotational distributions.

The main technique used to resolve the internal state distribution of the product OH has been laser induced fluorescence (LIF), which relies on detecting emission arising from the excited $A^2\Sigma^+$ state of OH which is populated by absorption of a photon, around

310 nm, from the ground $\text{OH}(^2\Pi)$ electronic state. In a prototypical LIF experiment⁵⁰, involving the measurements of the OH products of the $\text{O}(^1\text{D}) + \text{H}_2\text{O}$ reaction, the rotational distribution within the $\text{OH}(X^2\Pi; v=0)$ level was probed by exciting to the $\text{OH}(A^2\Sigma^+; v=1)$ state. For these measurements in the (1,0) vibrational band the R branch transitions, involving transitions for which $J_{\text{lower}} = J_{\text{upper}} - 1$, were found to be most free from interfering lines. In a similar fashion, the rotational distributions of the $\text{OH}(X^2\Pi; v=1,2)$ levels were probed by exciting the $\Delta v = +1$ vibrational bands of the $A^2\Sigma^+ \leftarrow X^2\Pi$ transition. A drawback in this and all other LIF measurements of OH is that the $\text{OH}(^2\Sigma^+)$ state predissociates, an event energetically possible beginning at $J=15$ of $\text{OH}(A^2\Sigma^+; v=1; J)$; however, fluorescence from $\text{OH}(^2\Sigma^+; v=1; J)$ continues to be observed up to rotational levels around $J \approx 27$ and LIF measurements in this regime are usually corrected for the effects of partial predissociation⁵¹. More severe restrictions on the number of measurable J states are present for determinations of populations of $\text{OH}(X^2\Pi; v=1-2)$. The radiative and predissociative lifetimes of $\text{OH}(A^2\Sigma^+)$ have been determined by Sutherland and Anderson⁵², who found that predissociation of this state occurs for $J > 22-23$ of $v=0$, for $J > 13-14$ of $v=1$ and all rotational states of $v=2$.

More recent corrections for predissociation have been determined by Brzozowski et al.⁵³. They measured most lifetimes of most of the states in the upper $A^2\Sigma^+$ level to a precision of ± 20 ns. The lifetimes of the $v=0$ level of the $A^2\Sigma^+$ state increase from 740 ± 20 ns in the lowest rotational level to just over 1 μs before the onset of predissociation, and decrease rapidly for rotational levels above the predissociation limit. The lifetime of the highest rotational level reported, $J=29$, was measured to be near 100 ns. The probabilities of predissociation were obtained by combining these lifetime measurements with theoretical estimates of the radiative probability in the absence of predissociation. These theoretical estimates were calculated by assuming a linear approximation for the dipole moment as a function of internuclear separation. By

matching the resulting predictions to the measured lifetimes of states below the predissociation limit, an optimum value for the slope of the dipole function was achieved for the range $1.0 \leq R_{\text{OH}} \leq 1.1 \text{ \AA}$ of $(-0.70 \pm 0.02) \text{ \AA}^{-1}$, in agreement with previous measurements⁵⁴ which yielded $(-0.716 \pm 0.006) \text{ \AA}^{-1}$ for this slope. Using the fitted dipole moment function, values were estimated for the radiative probabilities of states above the predissociation threshold and the difference between the theoretical radiative probability and the experimental emission probability was ascribed to the nonradiative predissociation channel.

In one variation the range of the LIF technique has been extended by Wiesenfeld et al. by probing off-diagonal transitions in the $\Delta v = -1$ band from 348-357 nm⁵⁵ or the $\Delta v = -2$ band in the region 384-409 nm⁵⁶. By exciting only to $v=0$ or 1 of the OH excited state, complete rotational distributions were determined for vibrational levels up to $v=3$ of the ground state for the OH product of the $\text{O}(^1\text{D}) + \text{H}_2$ reaction. Such techniques were hindered by uncertainty regarding the off-diagonal transition strengths.

Relaxation processes in both $\text{X}^2\Pi$ and $\text{A}^2\Sigma^+$ states of OH can affect the results of LIF studies. In many of the earlier studies of OH rotational distributions by LIF, bimodal rotational distributions were observed. The separate maxima were interpreted as resulting from two separate dynamical processes. In LIF studies of the $\text{O}(^1\text{D}) + \text{H}_2\text{O}$ reaction, however, Butler et al.⁵⁷ observed ~25% of the $v=0$ population in the low J levels, while Gericke and Comes⁵⁸ and Rodgers et al.⁵⁰ observed ~50% of the population in these levels. (The experiments of Gericke and Comes used a laser absorption technique, rather than LIF). Because all three groups reported different distributions, it was proposed by Butler et al. that the peaking in the low rotational levels was due to relaxation of the ground state OH, in spite of the fact that some of these experiments used nanosecond delays for the probe pulse and examined the products after only a fraction of a gas kinetic collision. Gericke and Comes reexamined this reaction⁵⁹ using isotopically

labelled H_2O at reduced pressures and were able to demonstrate that the low rotational levels were indeed a result of rapid rotational deexcitation. They presented strong evidence for collisions resulting in changes in rotational level with $\Delta J > 1$ in a later study⁽⁴⁾ of the rotational relaxation of OH by H_2O , in which they showed that translational and rotational thermalization of the excited OH occurred at a gas kinetic rate. This observation was rationalized by assigning a crucial role to the long range hydrogen bonding interaction between OH and H_2O . These "cold" portions of the rotational distributions were characterized by Boltzmann distributions having temperatures at or slightly above room temperature, instead of several thousand degrees Kelvin characteristic for the more populated higher rotational levels. Similar partially relaxed rotational distributions have been observed in LIF studies of $\text{O}(^1\text{D})$ with HCl ⁵⁷ and with NH_3 ^{61,62}, and here too may have been effects of a very efficient rotational relaxation mechanism. In contrast, early LIF studies of the $\text{O}(^1\text{D}) + \text{H}_2$ reaction⁵¹ showed no such rotational bimodality, and large pressures of buffer gases N_2 , He and O_2 in $\text{O}(^1\text{D}) + \text{H}_2\text{O}$ experiments⁵⁰ were shown to be relatively ineffective at rotationally relaxing the product OH. These results lead one to expect low rotational relaxation rates for gases without large dipole moments.

Similarly, collisional quenching depopulating the upper $\text{OH}(^2\Sigma^+)$ state is very dependent on the rotational level excited^{63,64} and the quenching efficiency tends to decrease with rotational excitation. Quenching has been shown to occur at larger than gas kinetic rates in experiments of Crosley et al.⁶⁵ involving laser excitation to specific rovibrational levels in the $\text{OH}(^2\Sigma^+)$ electronic state followed by time-resolved detection of the fluorescence as a function of the pressure of added gases. These rapid quenching rates were explained as being results of long-range attractive forces. With little rotational excitation, the reagents would be able to orient themselves along an approach involving a long-range well; however, should these attractive forces have a multipole character (i.e.

have specific angular characteristics) rotational excitation would decrease the effective attractive force and make close encounters which result in quenching less probable. The experimental quenching cross sections were found to correlate roughly with the probability of surmounting a centrifugal barrier and forming a complex. The latter theoretical cross-sections were calculated for an attractive interaction involving r^{-3} , r^{-4} and r^{-6} force constants for each reactant pair. The force constants themselves were calculated from known dipole and quadrupole moments, polarizabilities and ionization potentials. Rotational energy transfer within the excited $\text{OH}(A^2\Sigma^+)$ state was also observed in the preceding study and was most important for poor quenchers such as N_2 , which was observed to have a quenching rate constant of $(0.52 \pm 0.11) \times 10^{-10} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$. Over twenty different collision partners were examined: for CH_4 , HCl and H_2O the quenching rate constants for the $\text{OH}(A^2\Sigma^+; v=0; J=0)$ state were determined to be (3.1 ± 0.1) , (5.68 ± 0.06) and (7.9 ± 0.2) respectively, in units of $10^{-10} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$, while for the $\text{OH}(A^2\Sigma^+; v=0; J=7)$ state the measured quenching rates had decreased to (2.42 ± 0.08) , (5.03 ± 0.19) and (6.28 ± 0.16) respectively. One sees that an increase of 7 J-levels in the $\text{OH}(A^2\Sigma^+; v=0)$ state has decreased the quenching rate by a multiplicative factor of 0.78-0.88. Thus care ought to be taken to restrict the fluorescence detection to occur only under conditions of low reagent and buffer gas pressure for LIF measurements of rotational distributions, lest this rotational quenching dependence of the excited electronic state result in overestimating the population of higher J levels.

For example, the examination of the $\text{OH}(v=2-3)$ products of the $\text{O}(^1\text{D}) + \text{H}_2$ reaction by Wiesenfeld's off-diagonal LIF technique⁵⁶ and their earlier examination⁵⁵ of the $\text{OH}(v=1-2)$ products of the same reaction both used similar reagent mixtures: $(P_{\text{O}_3}, P_{\text{H}_2}, P_{\text{He}}) = (3, 100, 300) \text{ mTorr}$ and $(P_{\text{O}_3}, P_{\text{H}_2}, P_{\text{He}}) = (8, 100, 94) \text{ mTorr}$ respectively. If one assumes the concentration of H_2 in this experiment to be roughly steady-state (since initially $[\text{H}_2]_0 \gg [\text{O}_3]_0 > [\text{O}(^1\text{D})]_0$) then one may use Brzozowski's lifetime

measurements⁵³ and Crosley's quenching rates⁶⁵, as functions of rotational level in the $\text{OH}(A^2\Sigma^+;v=0)$ state, to estimate the effect of the decreasing quenching rate upon the amount of fluorescence actually detected in Wiesenfeld's LIF experiments. The radiative lifetime is roughly 750 ns for both $J=0$ and $J=6$, yielding a radiative rate constant $k_r = (750 \times 10^{-9})^{-1} = 1.3 \times 10^7 \text{ s}^{-1}$. The "pseudo first order" quenching rate constant for $J=0$ (assuming a nominal value of 298 K for the translational temperature) is $k_{q,J=0}[\text{H}_2] = (2.19 \times 10^{-10} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}) \times (0.1 \text{ Torr}) \times (3.24 \times 10^{16} \text{ molec} \cdot \text{cm}^{-3} \text{ Torr}^{-1}) = 7.1 \times 10^6 \text{ s}^{-1}$ while for $J=6$ it is $k_{q,J=6}[\text{H}_2] = (1.23 \times 10^{-10}) \times (3.24 \times 10^{15}) = 4.0 \times 10^6 \text{ s}^{-1}$. The competition between fluorescence and quenching will now be estimated, considering only the change in quenching ability of H_2 between rotational levels $J=0$ and $J=6$. For this simplified model of the competition between quenching and radiative rate constants, one has

$$\begin{aligned} [\text{OH}(X^2\Pi)]_r(t) &= \frac{k_r}{k_{q,J}[\text{H}_2] + k_r} [\text{OH}(^2\Sigma^+;v=0;J)]_0 \{1 - \exp(-(k_{q,J}[\text{H}_2] + k_r)t)\}, \\ \text{and} \\ [\text{OH}(X^2\Pi)]_q(t) &= \frac{k_{q,J}[\text{H}_2]}{k_{q,J}[\text{H}_2] + k_r} [\text{OH}(^2\Sigma^+;v=0;J)]_0 \{1 - \exp(-(k_{q,J}[\text{H}_2] + k_r)t)\}, \end{aligned}$$

where $[\text{OH}(X^2\Pi)]_r(t)$ and $[\text{OH}(X^2\Pi)]_q(t)$ are the concentrations of radiatively produced and quenched ground state products respectively. Clearly a constant percentage of the upper state population fluoresces from a given J level at all times during the evolution of this fluorescence, and is thus independent of the gate width of the detection electronics. For the $J=0$ level of the upper state, the percentage of the upper state fluorescing is given by $(1.3 \times 10^7) / (1.3 \times 10^7 + 7.1 \times 10^6) \times 100\% = 65\%$, and for the $J=6$ level $(1.3 \times 10^7) / (1.3 \times 10^7 + 4.0 \times 10^6) \times 100\% = 76\%$ of the population of the upper state fluoresces. This crude estimate indicates that ground state LIF populations which use the $\text{OH}(^2\Sigma^+;v=0;J=6)$ state to fluoresce will be overestimated by close to 16% relative to populations determined using the $\text{OH}(^2\Sigma^+;v=0;J=0)$ state. If the decrease in quenching

rate continues up to the highest J-levels and results in negligible quenching as compared with radiative transitions, then one might expect to see very high rotational levels overestimated by up to $(100\%-65\%)/65\%$, or about 50%, relative to the lowest rotational level, at the reagent pressures used in Wiesenfeld's experiments.

Indeed Wiesenfeld discussed the possibility of such effects in the most recent of his papers⁵⁶ involved in the preceding calculation, but claimed that "Once again, the pressures used in the present experiments were sufficiently low to preclude the possibility of significant perturbations being introduced by quenching of any of the $\text{OH}(A^2\Sigma^+)$ rotational levels." The only pressure dependence reported in this paper involved spectra taken with 8 Torr of He buffer gas (with the same partial pressures of O_3 and H_2). As he expected, he found rapid rotational relaxation for ground state levels up to $J \gg 6$, at which point the energy difference between rotational energy levels exceeds kT and slower rotational energy transfer occurs with the He buffer gas. The presence of high rotational levels of $\text{OH}(X^2P)$ at high He pressures and at high delay times before the LIF probe was taken to be an indication of metastability of higher rotational levels. They found that the high rotational levels of higher vibrational states were relaxed more efficiently. Considering also the decreasing amount of rotational excitation (for energetic as well as dynamical reasons) in higher vibrational states, it was suggested that chemiluminescence methods, "which depend on achieving thermal rotational distributions ... must include consideration of the collisional metastability of the highly excited levels populated by ..." [the $\text{O}(^1D) + \text{H}_2$ reaction].

Three rebuttals seem appropriate. First, the chemiluminescence methods do not rely on achieving equilibrium between the rotational states. All chemiluminescence is measured. Any apparent "restrictions" of chemiluminescence measurements to low rotational levels occur because the population, if any, of the higher rotational levels is simply too small to be seen at the signal-to-noise ratio of the spectrum. Neither is the

apparent dearth of high rotational levels a result of less favorable A-factors: the A-factors for the strong P-branch of OH actually increase with rotational level. In fact, in measurements of HF distributions of products of the $O(^1D) + CH_3F$ reaction, rotational levels up to $J=26$ were detected at the earliest time delay⁶⁶.

Second, one must be wary when extrapolating results based on quenching with He to the more complex chemical environment of the chemiluminescence measurements. The "buffer" gases in the experiments of this thesis consisted mainly of the reagents, O_3 and RH, photolysis products, $O(^3P)$ and O_2 , and any reaction products. No rare gas buffer gas was used. In view of the internal energy level structure of most of these collision partners as compared with He, it would be extremely surprising if rotational relaxation continued to be restricted to the lowest ($J \leq 6$) levels as Wiesenfeld found for He. The chemiluminescence experiments involve collision partners expected to be much more efficient than He at causing rotational relaxation.

Third, the data upon which Wiesenfeld's recommendation was based was itself suspect as shown by the short calculation presented earlier. Any errors in the LIF experiment, which might reasonably increase the apparent populations of high rotational states by ~50%, would tend to overestimate populations of the lower vibrational levels, in which these high rotational states are most prevalent. To summarize, many of the LIF experiments to date possibly underestimate the degree of vibrational inversion because of changes in the $OH(^2\Sigma^+;v;J)$ quenching rates while the chemiluminescence experiments possibly overestimate vibrational inversion if very low, but broad, distributions of the population in high rotational levels of the lower vibrational states were missed.

The disadvantages of the LIF method are offset by the innate sensitivity inherent in fluorescence detection methods as compared with absorption techniques⁶⁷ and the general applicability of LIF to a wide range of molecules. An example is provided by the study of the $O(^1D) + HCN$ reaction by Wiesenfeld et al.⁶⁸. The predominant products

are $\text{NH}(a^1\Delta) + \text{CO}(X^1\Sigma^+)$, while 10% of reactive encounters form $\text{OH}(X^2\Pi) + \text{CN}(X^2\Sigma^+)$. Not only were they able to determine the populations of $\text{OH}(v=0,1)$, but they were also able to probe the populations of $\text{NH}(a^1\Delta)$, $\text{NH}(X^3\Sigma^-)$, $\text{CN}(X^2\Sigma^+)$, $\text{CN}(A^2\Pi)$ and $\text{NCO}(\tilde{X}^2\Pi)$. By varying the time delay of the probe LIF pulse, the population of the $\text{NH}(X^3\Sigma^-)$ ground state was shown to be a result of a secondary reaction which was presumed to be that of CN with either O_3 or $\text{O}_2(a^1\Delta)$. The absence of prompt $\text{NH}(X^3\Sigma^-)$ production, in spite of favorable exothermicity, was interpreted as a consequence of spin conservation. Like OH, the LIF signal from the $\text{NH}(c^1\pi \leftarrow a^1\Delta)$ transition was absent for $\text{NH}(c^1\pi; v>1)$ because of predissociation. Production of $\text{CN}(A^2\Pi)$ was endothermic, and no LIF from the $B^2\Sigma^+$ state could be induced. Vibrational levels of $\text{CN}(X^2\Sigma^+)$ up to $v=3$ could be probed using various vibrational bands of the $B^2\Sigma^+ \leftarrow X^2\Sigma^+$ transition. Lastly, the $\text{NCO } \tilde{B}^2\Pi \leftarrow \tilde{X}^2\Pi$ and $\tilde{A}^2\Pi \leftarrow \tilde{X}^2\Pi$ transitions were used to probe the NCO energy distribution. It was found that $\text{NCO}(\tilde{X}^2\Pi)$ only appeared on a time scale ten times longer than that associated with primary products of the $\text{O}(^1\text{D}) + \text{HCN}$ reaction.

The UV laser absorption technique of Gericke and Comes^{59,69} used the same electronic transitions as the LIF studies, but circumvented the problem of predissociation in the upper $\text{OH}(^2\Sigma^+)$ state. They were able to measure complete rotational distributions for the $\text{OH}(X^2\Pi; v=0,1,2)$ vibrational states produced in the $^{16}\text{O}(^1\text{D}) + \text{H}_2^{18}\text{O}$ reaction. Both laser absorption and LIF techniques are capable of the high spectral resolution required to accomplish separation of the isotopic ^{16}OH and ^{18}OH spectra. Gericke and Comes found that it was predominantly the newly formed ^{16}OH which was formed in vibrationally excited states, with a vibrational distribution of $P_{\text{OH}}(v=0:1:2) = 69: 22: 9$, while the previously existing ^{18}OH bond was produced almost exclusively in the ground vibrational state ($P_{\text{OH}}(v=0:1:2) = 92: 8: <1$). Analogous LIF studies⁵⁷ using isotopically labelled H_2O agreed with these ratios as far as the $v=1$ and 2 levels were concerned, within the estimated errors for the LIF experiment.

One of the early investigations of $O(^1D)$ reactions also used a UV absorption method to detect $O_2(^1\Sigma_g^+)$, $O_2(^1\Delta_g)$, $ClO(^2\Pi)$ and $OH(^2\Pi)$ products of reactions with NH_3 , H_2 , HCl , CH_4 and H_2O . These studies of Basco and Norrish⁷⁰ were accomplished using a 20-25 μs photolytic flash producing $O(^1D)$ from ozone. The initiation of the photolysis flash was followed (often overlapping the photolysis pulse itself) by a time delayed spectroscopic flash of shorter duration whose absorption was monitored in the 250-560 nm spectral range by a spectrograph equipped with sensitive photographic plates. The partial pressures of the reagents were 4-6 Torr of ozone, 4-150 Torr of RH reagent, and 150-200 Torr of N_2 buffer gas. At such pressures even the earliest time delay of 3.5 μs corresponds to many thousand gas kinetic collisions, giving ample opportunity for vibrational relaxation and secondary reactions to influence the results. They found that the product OH was produced in at least each of the lowest three vibrational levels for reactions of $O(^1D)$ with H_2 , H_2O , CH_4 and NH_3 . In the CH_4 absorption experiment, faint bands on a continuous background were seen at all time delays after the photolysis flash and were attributed to formaldehyde. The strong absorption of the NH radical was seen to decay relatively slowly. In the HCl reaction, the OH absorption was weak while that of ClO was strong. The strong ClO signal was attributed to the secondary $Cl + O_3$ reaction, which produces ClO and O_2 .

Molecular beam techniques have been used to determine product angular and velocity distributions using time-of-flight mass spectrometry. In these molecular beam techniques, a cross-correlation time-of-flight method was employed to determine the velocity distributions of the products. The reactions of $O(^1D)$ with CH_4 ⁷¹, H_2 ⁷² and HD ⁷³ have been studied using beam techniques. These experiments used an rf discharge of O_2 in He to produce $O(^1D)$. In the experiments with CH_4 , the CH_3O and CH_2O products at masses 30 and 31 were analyzed in a rotatable, quadrupole mass spectrometer and the CH_2O was suggested to be a fragmentation by-product produced in the ionizer of

the mass spectrometer and not in the $\text{O}(^1\text{D}) + \text{CH}_4$ reaction itself. In the $\text{O}(^1\text{D}) + \text{H}_2$ experiments, the OH product distribution was analyzed. It was found to be symmetrically peaked in the center of mass frame of reference. The OH product was found to deposit ~20% of its available energy into translation.

More classical chemical techniques combined with gas-liquid chromatographic and mass spectroscopic methods of analyzing the long-term reaction products have also been used successfully by Cvetanovic et al.. These techniques involved long exposures of mixtures containing N_2O to repeated photolytic flashes, using a mercury lamp at 184.9 nm or zinc lamps at 213.9 nm, which produced low concentrations of $\text{O}(^1\text{D})$. By controlling the reagent pressures and adding radical scavengers as appropriate, they were able to test the validity of possible reaction mechanisms leading to their observed product yields. In an early paper⁷⁴, the reaction of $\text{O}(^1\text{D})$ with propane ($\text{CH}_3\text{CH}_2\text{CH}_3$) was investigated. The observed reaction products were classified into three groups: (1) insertion products forming the collisionally stabilized alcohol (*n*-propyl or isopropyl alcohol), (2) abstraction products formed by recombination of radicals produced when OH is formed as a primary reaction product (2,3-dimethyl-butane, 2-methylpentane, and *n*-hexane), and (3) other alkanes, attributed to end products of C-C bond cleavage in the "hot" intermediate alcohol. They observed a continuous increase in the yields of the stabilized alcohols as pressure was raised up to the pressure limit of ~1200 Torr imposed by their reaction vessel. This increase in the yield of the alcohol was inferred to be a result of collisional stabilization of a "hot" intermediate alcohol: excess energy in the initially formed complex which would otherwise have resulted in the cleavage of a C-OH bond (mechanism 2) or a C-C bond (mechanism 3) was removed in collisions as internal or translational excitation of the collision partner, leaving insufficient internal energy in the alcohol for dissociation. Moreover, they observed that $\text{O}(^1\text{D})$ was indiscriminate about the C-H bond into which it inserted, while $\text{O}(^3\text{P})$ preferentially attacked the weaker

secondary C-H bonds. Based on this difference, the relative quenching abilities of Xe, N₂ and Kr were determined to be 0.47, 0.15 and 0.05 respectively, expressed as a fraction of the total reaction rate with O(¹D). He and SF₆ were shown to be very poor quenchers of O(¹D). Cvetanovic et al. later⁷⁵ investigated the O(¹D) + (CH₃)₃CH reaction. They found O(¹D) attack on each hydrogen of isobutane to be equally probable. When the pressure was raised, the yield of butanols increased and saturated at a pressure of ~1000 Torr. The "hot" alcohols formed as intermediates in the insertion process were stabilized at a pressure much lower than the several thousand Torr necessary to stabilize the hot propanols of the preceding investigation. They calculated the mean lifetimes of the hot butanol intermediates to lie between 200 and 500 ps, while the lifetime of the propanol intermediate was estimated to be shorter, around 10 ps. The increased lifetimes of the larger alcoholic intermediates are a result of the increased density of states available to the intermediate. As in unimolecular RRKM theory, a longer time is then expected before the (assumed) statistically distributed energy of the complex will redistribute itself and put more than the threshold amount into a local mode which results in the formation of reaction products. In the isobutane experiment when pressures were increased past the saturation pressure for complete stabilization of the intermediate alcohol, products of the "abstraction" channel still persisted. This was understood as the result of a fraction of reactive encounters leading to OH formation without ever forming a C-O bond; i.e., a fraction of the reactive collisions proceeded entirely in an O-H-R geometry. Extensions of this work to neopentane⁷⁶ (C(CH₃)₄) showed that this reaction has an intermediate alcohol which was stabilized at only 150 Torr. The mean lifetime of the intermediate was thus very long (4 ns). In this reaction, ~25% of the reaction was abstractive, forming OH without passing through ROH geometries while the formation of neopentanol accounted for ~66% of the reaction above the saturation pressure. Similar results were found for cyclopentane⁷⁷, with a mean

lifetime for the excited alcohol of 1.7 ns and a saturation pressure for formation of stabilized main cyclopentanol product of ~ 200 Torr, and with abstraction accounting for $\sim 20\%$ of reactions, and a third possibility, molecular elimination of H_2 , occurring $\sim 10\%$ of the time.

Chemiluminescence techniques too have been used to probe the vibrational product distribution. These techniques typically rely on the detection of the infrared spontaneous emission between $2500\text{--}3600\text{ cm}^{-1}$ resulting from $\Delta v = -1$ transitions of $OH(^2\Pi; v=1\text{--}5)$. Unfortunately, the very low transition rates ($\sim 12\text{ s}^{-1}$) make such measurements difficult. Early applications in this laboratory^{78,79,80} presented partially relaxed distributions — lower bounds to the actual initial vibrational inversion. These measurements employed low pressure flow systems to minimize relaxation and estimate the initial vibrational distribution.

One chemiluminescence study⁷⁸ investigated the $O(^1D) + H_2$ reaction and reported vibrational distributions of the OH product at several pressures. At the lowest pressure used, $(P_{O_3}, P_{H_2}) = (25, 10)$ mTorr, a mildly inverted product vibrational distribution which peaked in $OH(v=2)$ was observed. This distribution was measured to be progressively more relaxed as the total pressure for the reaction, with the same O_3/H_2 ratio, was increased to a maximum of 800 mTorr. The half-life of the emission was about 2 ms, so it was judged that considerable vibrational deexcitation had already occurred in the measured vibrational distributions. In this study, energetic considerations of earlier LIF rotational distributions and molecular beam measurements of the translational energy release were used to show⁷⁸ that the "rotational excitation must decrease rapidly with increasing vibrational level." With a preliminary version of the time-resolved chemiluminescence apparatus used in this thesis, a later reexamination⁸¹ of the $O(^1D) + H_2$ reaction also resulted in a mildly inverted OH distribution which peaked in $OH(v=2)$.

Another chemiluminescence study⁷⁹ involved the $O(^1D) + CH_4$ reaction and demonstrated a distribution slightly inverted and peaking in $OH(v=2)$ to be a lower limit for the vibrational distribution of the product OH. $OH(v=4)$ was populated, that being the maximum level allowed energetically. The most inverted vibrational distribution was obtained at the lowest reagent pressures, $(P_{O_3}, P_{CH_4}) = (5.5, 5.6)$ mTorr. Luntz's LIF study of this reaction⁸² used partial pressures of $(P_{O_3}, P_{CH_4}, P_{Ar}) = (1, 10, 2000)$ mTorr. At his probe time delay of $0.5 \mu s$ he calculated that the $O(^1D)$ in his experiment underwent ~ 5 collisions with Ar before reacting with his reagent. The relative kinetic energy of the $O(^1D)/CH_4$ collision was ~ 5.8 kJ/mol in Luntz's experiments. Because no buffer gas was used in the chemiluminescence measurements since the available pumping speed was limited, and because the gas kinetic reaction rate allowed little opportunity for translational equilibration, the relative kinetic energy in the $O(^1D)/CH_4$ collision was estimated to be ~ 23 kJ/mol in the chemiluminescence experiment. The chemiluminescence paper pointed out that the increased collisional energy would result in increased sampling of abstractive geometries which could conceivably contribute to the vibrational inversion seen in that experiment. The higher translational energy for $O(^1D)$ was also available to the reactions presented in this thesis, which were all done at reagent pressures of $(P_{O_3}, P_{RH}) = (10, 10)$ mTorr, with no additional buffer gas.

In investigations⁸⁰ of the $O(^1D) + H_2S$ reaction, infrared emission from all five energetically allowed vibrational levels of OH was seen. The most inverted distributions were peaked in $OH(v=3)$ and were obtained at the lowest (10 mTorr) total pressures employed. This observation was combined with an earlier LIF measurement⁸³ which gave $P_{OH(v=1)}/P_{OH(v=0)} = 0.17$ to suggest that the OH vibrational distribution was "strongly bimodal." Again the caveat regarding the higher translational energy of the $O(^1D)$ atom in the chemiluminescence measurements was noted⁸⁰.

The measurements presented in thesis were obtained using the chemiluminescence technique in a time-resolved modification which will be detailed in the next chapter. Chemiluminescence studies of the $O(^1D) + HCl$ and $O(^1D) + HBr$ reactions will be presented. The $O(^1D)$ reactions with H_2S and CH_4 , which were previously investigated using the low pressure flow system, have also been investigated using the time-resolved technique. As is wont with chemiluminescence measurements, no information regarding the lowest energy level is obtained. Thus the vibrational distributions presented in this thesis contain no information about the populations of $OH(v=0;J)$ levels. In general, the time resolution of such techniques has been lower than that of LIF techniques, so that rotationally relaxed vibrational distributions have been measured.

(2.2) General Dynamics of $O(^1D) + RH$ Reactions

A dynamical understanding of $O(^1D) + RH$ reactions hinges upon a knowledge of the features of the potential energy surfaces involved. Figure 20 represents various triplet and singlet surfaces connecting the reagents and products, ignoring any possible structure in the R group. The upper half depicts reaction along the collinear O-H-R $C_{\infty v}$ geometry while the lower half represents an insertion mechanism, forming R-O-H in C_s symmetry, which subsequently dissociates. This figure will now be discussed in detail.

The most important feature of such reactions is the strong well corresponding to ground state H-O-R ($\tilde{X}^1A'$) at a tetrahedral bond angle of $\sim 102^\circ$. This electronic state correlates with the $O(^1D) + RH$ reagents and is the principal reactive surface. The extension of the deep $\tilde{X}^1A'$ ROH well far into the entrance channel gives rise to large cross sections for the $O(^1D)$ reactions. The $\tilde{X}^1A'$ surface has no barrier for insertion geometries: no activation energy is found for many of these reactions.

Figure 20: Qualitative energy level diagram for the $\text{O}(^1\text{D}) + \text{HR} \rightarrow \text{OH} + \text{R}\cdot$ reaction. The lower portion displays the singlet and triplet states near the equilibrium geometry corresponding to the stable HOR molecule. The upper portion represents the energetics of a collinear $\text{O} \rightarrow \text{HCl}$ approach, showing the C_s states which correlate with these $\text{C}_{\infty v}$ geometries in parentheses.

The $^3\Pi$ collinear ground state is also well characterized through studies of $O(^3P) + HR \rightarrow OH + R\cdot$ reactions. Barriers on the collinear O-H-R triplet surface are typically 8-32 kJ/mol, depending on the R-H bond strength. It should be noted that since the $C_{\infty v}$ geometries form a subset of the C_s geometries, the actual, multidimensional potential energy surfaces exhibit a smooth transition between the collinear and insertion energetics. The C_s H-O-R states which correlate with the $C_{\infty v}$ O-H-R states are indicated in the upper portion of figure 20. The two lowest triplet surfaces in C_s symmetry ($^3A''$ and $^3A'$) become degenerate in $C_{\infty v}$ symmetry, both correlating with the $^3\Pi$ collinear surface. The vertical transition energies to the $^3A''$ and $^3A'$ surfaces are known for many ROH species through absorption spectra or *ab initio* calculations and show that the barriers on the $^3A''$ and $^3A'$ surfaces are much higher than the barrier on the $^3\Pi$ surface. As a result (see figure 20), any systems on the lowest two triplet surfaces are predisposed towards collinear reaction geometries.

The two lowest excited singlet states ($^1A''$ and $^1A'$) in C_s symmetry both correlate with the $^1\Pi$ $C_{\infty v}$ surface. The $\tilde{X}^1A'$ ground state correlates with the $^1\Sigma^+$ collinear O-H-R state, which correlates with an excited $OH(A^2\Sigma^+)$ product. The $^1\Sigma^+$ electronic state of O-H-R thus has a high barrier. Reaction on the singlet manifold in collinear O-H-R geometries will instead favor the lower energy $^1\Pi$ surface, which does not have a large barrier. This $^1\Pi$ surface splits into two excited singlet states of $^1A'$ and $^1A''$ symmetry for non-collinear approaches. Therefore there is an avoided crossing between the excited and ground states of $^1A'$ symmetry for near-collinear O-H-R geometries. This implies that as one approaches near-collinear geometries on the ground state surface what actually occurs will be a transition to the $^1A'$ electronic state correlating with the $^1\Pi$ collinear symmetry. Alternatively, this implies that trajectories which deviate far enough from a near-collinear approach on the $^1A'$ surface which correlates with the lower energy $^1\Pi$ collinear O-H-R surface will experience a transition

to the ground state $\tilde{X}^1A'$ surface. Once on this surface, the O_{HR} system will experience strong forces (i.e. a very steeply sloped potential surface) favoring insertion geometries. This change in slope of the potential energy surface (p.e.s.) at this avoided crossing is one of the difficulties in analytical representations of $O(^1D) + RH$ surfaces.

The $\tilde{X}^1A'$ surface undergoes entrance channel crossings with potential surfaces originating from the $O(^3P) + RH$ reagents. Since for more collinear configurations the barrier on either triplet surface will decrease and the energy of the singlet surface will rise, the crossing of the $\tilde{X}^1A'$ and $^3A''$ (or $^3A'$) ground state surfaces will occur later in the entrance channel and will have a decreased angle of the surface intersection. Thus a more collinear entrance channel geometry implies that the singlet and triplet surfaces will be nearby for a larger region of phase space and leads one to expect such a crossing to be more favorable; however, this singlet-triplet crossing on the lowest electronic surfaces has not been found to be important for small RH groups such as diatomics. This point will be discussed further in the $O(^1D) + HCl$ chapter.

Regarding larger $R\cdot$ groups, the early studies of Cvetanovic et al.^{74,75,76,77} showed that as the size of an alkyl $R\cdot$ group was increased, an increasing fraction of this reaction could not be quenched by pressure to form a stable ROH alcohol. This observation was explained by assuming that a component of the reaction proceeded rapidly, without the formation of a complex. This unquenchable component was hypothesized to react directly, along O-H-R geometries. Such near-collinear collisional dynamics is termed "abstraction" and, because the exit channel is also near-collinear and exerts little torque about the center of mass of the diatomic product, the products of abstraction reactions will exhibit little rotational excitation: instead, translational or vibrational excitation is favored. On the other hand "insertion" reactions, proceeding through H-O-R geometries to a bent exit channel with corresponding large torques exerted about the center of mass of the product diatomic, generally exhibit high rotational

excitation. In more recent LIF studies of $O(^1D) + RH$ reactions for $RH = \text{alkanes}$ ⁸² and $RH = H_2$ ⁸⁴, Luntz analyzed the bimodality of the rotational distributions of the $OH(v=0-1)$ products, classified reactions as abstractions (low rotational states) or insertions (high rotational states), and assigned the abstraction component to be an effect of the entrance channel singlet-triplet surface crossing. The production of high rotational states was consistent with a bent exit channel geometry as favored by ground state X^1A' insertion reaction. In agreement with Cvetanovic's results, Luntz found the abstraction component to be more important for larger hydrocarbons: the fractions of abstraction events for H_2 , CH_4 , C_2H_6 , C_3H_8 and $C(CH_3)_4$ were measured to be 0%, 5%, 20%, 70% and 90% respectively. For hydrocarbons larger than methane, Luntz found the vibrational distribution of this abstractive component increasingly favored $OH(v=0)$. This was interpreted to be a result of the ability of the larger R groups to better absorb more of the reaction's exothermicity in internal excitations. (Luntz also applied this interpretation to explain features of his experiments⁸⁵ with $O(^3P)$ and alkanes). The rotational distribution of $O(^1D)$ abstraction component was similar to that produced in reactions of $O(^3P) + HR$, which was known to favor a collinear O-H-R reaction path. Luntz also suggested that, much as the increased density of states in large molecules promotes intersystem crossings, larger R groups are more likely to be influenced by this surface intersection. Although the correlation diagram shows only one singlet-triplet crossing, the full potential will have multiple crossings, corresponding to each RH internal coordinate. As implied above, the $C_{\infty v}^3\Pi$ surface, which connects to both $^3A''$ and $^3A'$ states in C_s geometry, has a decreased barrier to reaction. This favors linear exit channel geometries for reactions that do cross onto the triplet manifold — hence the classification of the rotationally colder product as a result of abstractive dynamics would indeed be appropriate.

One may be tempted to criticize Luntz's conclusions by suggesting: (1) that fast rotational relaxation was the real cause of his apparent abstraction component, or (2) that roughly 10% of the photodissociation of ozone produces $O(^3P)$ directly, which will be translationally excited and undergo fast reaction with RH wholly on the triplet surface. However, most of these reactions were run at similar reagent pressures of (P_{O_3} , P_{RH} , P_{Ar}) = (1, 10, 2000) mTorr, so both suggested criticisms would result in effects which were similar for each of the alkanes. Furthermore, the fact that he was able to see reactions with very little abstraction component argues against the possibility of fast rotational relaxation having occurred and the fact that 2 Torr of buffer gas was used implies that both $O(^1D)$ and $O(^3P)$ translational energies would, on average, be substantially reduced before collisions with the minor alkane component of the reagent gas mixture and before the time delay of 0.5 μ s for the LIF probe. This would further discriminate against the $O(^3P)$ reaction being directly involved in Luntz's observations, since $O(^3P)$ reaction rates are generally many orders of magnitude lower than the rates of $O(^1D)$ reactions.

The RH reagents studied in this thesis (HCl, HBr, H_2S and CH_4) are not larger than CH_4 , so neither the ground state surface crossing resulting in abstractive reactions nor the decreased vibrational excitation of the OH product as a result of internal excitation of the $R\cdot$ reaction product is expected to be a factor.

Luntz also investigated⁸² the fine structure components of the product OH. The $OH(^2\Pi)$ product exhibits spin-orbit coupling, between the spin and electronic angular momenta, which splits each (v,J) state into $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ components. Both these spin doublets are populated within the statistical ratio (within $\pm 10\%$) in typical $O(^1D) + RH$ reactions. This contrasts with $O(^3P)$ reactions, where the lower spin doublet states may be twice as likely to be formed as the upper ones⁸⁵.

Each of these components exhibits a further, smaller Λ doubling into Π^+ and Π^- states due to orbital-rotational coupling. In, and only in, the limit of high rotational states, the Π^+ state may be associated⁸⁶ with a molecule whose singly occupied π orbital lobes are directed in the plane of rotation of the molecule, rather than perpendicular to the plane of rotation (Π^-). Many of the rotational distributions do exhibit high rotational states in the $\text{OH}(^2\Pi; v=0)$ product and have shown preferential population of the Π^+ state. This indicates that the singly occupied orbital which results from the R-O bond cleavage lies in the plane of rotation of the product OH molecule. If one neglects for the moment any dynamical constraints on the velocities of the exiting O and H atoms, considering them to be initially at rest for example, then this implies that the exit channel forces lie in a plane containing the R-O bond: such forces acting on the oxygen atom increase the rate of rotation of OH about its center of mass. For polyatomic R groups, however, (in this simplified model still) torques on the exiting OH may be generated out of the plane of the R-O-H entity and can populate Π^- states of high rotational levels of the OH product. In the more general model, the exiting O-H may already possess high velocities resulting from incipient rotational energy. For example, if the OH is rotating strongly nearly perpendicularly to the R-O repulsion in the product channel transition state, then one might expect the Π^- state to be populated instead. Strong Λ doublet selectivity favoring the Π^+ state was observed by Luntz in LIF studies of the $\text{O}(^1\text{D}) + \text{H}_2$ reaction⁸⁴, which can adequately be explained by the simple model above. However, the success of the simple model could be only fortuitous: for the related $\text{O}(^1\text{D}) + \text{HCl}$ reaction, Luntz later observed that both Λ doublets were populated equally even though the R· group was monatomic. Luntz suggested that one reason for the difference in selectivity might be the much larger initial orbital angular momentum, but failed to provide a mechanism for this suggestion. In fact, such a dynamical difference arising from angular momentum considerations is believed by the author to be the root of this

difference in Λ doublet selectivity between the $O(^1D) + H_2$ and $O(^1D) + HCl$ reactions. The explanation is based on the implications of angular momentum constraints on dissociations described by RRKM methods and will be presented in the $O(^1D) + HCl$ chapter.

The mechanism for the quenching channel producing $O(^3P) + HR$ has been suggested above to not involve the surface crossings of the lowest singlet and triplet states. The possibility of involvement of the first excited triplet ($^3A'$) and singlet ($^1A''$) surfaces was only recently noted⁴³ as a possible source of the high vibrational inversion present in the HCl product of the $O(^1D) + HCl \rightarrow O(^3P) + HCl^\dagger$ quenching channel and will be discussed in detail in a later chapter. The energies of the excited $^3A'$ and $^1A''$ states for HOCl were calculated by CI techniques by Bruna et al.⁸⁷ and found to be separated by ≈ 18 kJ/mol at the equilibrium geometry. The surfaces remained in close proximity for a large range of geometries. The extent of involvement of this excited state pathway depends upon the particular R· group, since the close proximity of the $^3A'$ and $^1A''$ excited states for large regions of configuration space is not a general feature: for many R-OH compounds, these states may be much higher in energy than the $O(^1D) + RH$ asymptote⁸², and thus cannot be involved in reactive dynamics. In comparison with the lowest $^3A''$ state, the excited $^3A'$ triplet state displays a more repulsive exit channel and in $C_{\infty v}$ O-H-R geometries, since it becomes degenerate with the lower energy $^3A''$ state which itself favors collinear O-H-R geometries, displays an even stronger predilection for linear exit channel geometries. With a monatomic R group then, a quenching mechanism involving this excited $^3A'$ state would especially be expected to channel the reaction exothermicity into vibrational H-R excitation. Previously, reaction has been considered to occur on the $\tilde{X}^1A'$ ground state surface. The suggested involvement of the excited $^1A''$ state also gives rise to a new possibility for reaction if the intermediate on the $^1A''$ or $^3A'$ surface dissociates to $OH(^2\Pi) + R\cdot$ instead of the

observed $O(^3P) + HR$ quenching product. Since both $^1A''$ and $^3A'$ excited states favor linear geometries, the OH product of this alternative channel should also display a marked vibrational inversion as a result of a more collinear O-H-R exit channel.

The suggestion that excited states be involved in $O(^1D)$ reactions is not novel. The involvement of alternative reaction mechanisms involving excited states has been noted in other $O(^1D)$ reactions. For example, in the reactions of $O(^1D)$ with CHX_3 ($X = F, Cl$), the $HX + OCX_2$ product channel has been shown to populate the $OCX_2(\tilde{X}^1A_1)$ and $OCX_2(\tilde{A}^1A_2)$ states in chemiluminescence studies⁸⁸. In this study, it was found that the $CHCl_3$ reaction yielded approximately equal quantities of CO and HCl while the CHF_3 reaction yielded no observable CO emission. This observation could be explained by the different behaviors of the $OCX_2(\tilde{A}^1A_2)$ product: $OCCl_2(\tilde{A}^1A_2)$ predissociated while $OCF_2(\tilde{A}^1A_2)$ did not.

CHAPTER 3

(3.1) General Considerations

The mathematical basis of Fourier Transform Spectroscopy (FTS) lies in the Wiener-Khintchine Theorem⁸⁹. Simply put, this theorem states that the Fourier transform of the autocorrelation function of a time series yields the power spectrum of that variable.

The time series, $y(t)$, must be statistically stationary: its autocorrelation function, $K(t_1, t_2) \equiv \langle y(t_1)y(t_2) \rangle$, must be a function only of the time difference, $K(t_1, t_2) = K(t_2 - t_1)$. In particular, the mean square value, $\langle y^2(t) \rangle$, of the time series must already have achieved its equilibrium, or stationary, value. For Fourier Transform Infrared (FTIR) spectroscopy, the pertinent time series is the electric field of a source of infrared radiation.

The autocorrelation function of the radiation is measured using a Michelson interferometer. The speed of the Fast Fourier Transform (FFT) algorithm is desirable for the computation of the power spectrum. This requires that the autocorrelation function be sampled at equidistant points or, equivalently, that the detector signal be digitized at equidistant positions of the moving mirror of the interferometer. This is accomplished by sending a monochromatic laser beam through the same interferometric process as the radiation of interest. A separate photodetector then detects a cosinusoidal signal as a function of the position of the moving mirror, with zeroes occurring every time the optical path difference changes by $\lambda_{\text{ref}}/2$, where λ_{ref} is the wavelength of the reference laser. Typically, a HeNe reference laser is used to provide this measure of changes in the optical path difference (the "retardation") of the two interfering beams.

For the purposes of coordinating the data collection, a white light beam in the interferometer is also monitored separately. After the interferometric procedure the

signal from this beam exhibits significant amplitude only when the optical path lengths traversed by the split beams of white light are nearly equal. When these two optical path lengths are the same, all frequencies combine constructively to yield a sharp maximum intensity on the white light detector. The mirror position at which this occurs is called the zero path difference (ZPD).

The fundamental frequency range of the resulting spectrum is determined by the distance between the points sampled in the interferogram: the Nyquist theorem requires the sampling of any sinusoidal waveform at least twice per period in order to unambiguously determine its frequency. In accord with this principle, wavelengths outside the fundamental frequency range are folded back, or aliased⁹⁰, into the fundamental spectral bandwidth.

The resolution of the spectrum is determined by the maximum optical retardation achieved during the acquisition of the interferogram. This may be understood to be a result of the convolution theorem, which states that the Fourier transform of a product of two functions is the convolution of the Fourier transform of the functions. Sampling a finite range of optical retardation corresponds to multiplying the true (infinitely long) interferogram by a rectangle function. This implies that any single, pure frequency will have a lineshape given by the Fourier transform of the rectangle function. The full width at half maximum (FWHM) of this lineshape is inversely proportional to the breadth of the rectangle function, and determines the minimum separation between two spectral lines of equal intensity before separate peaks may be resolved. For further details about the mathematical aspects of the analysis of the resulting interferograms the reader is referred to any of several standard texts^{90,91,92}.

There are several methods which have been used to acquire time-resolved FTIR spectra. Which method is appropriate depends on the time scales of the interferometer scan and the event to be monitored. The method used in this laboratory was first reported

by Sloan et al.⁹³ in 1986. For information regarding various other implementations of time-resolved FTS, a more detailed account of the modified version of this method and an overview of areas to which time-resolved FTS has been applied, the reader is referred to a review article by Sloan and Kruus⁹⁴. This article also describes pitfalls present in early implementations of the "sorting" method of time-resolved FTS. When poorly implemented, this method of time-resolved spectroscopy initially resulted in spectral artifacts⁹⁵ which were not recognized as such until many years later⁹⁶. Such effects are minimized in the method used in this thesis.

In the experiments of this thesis, the mirror of the interferometer moved significantly during the acquisition of any single transient event but was yet not fast enough to record an entire scan during any one event: the transient took roughly 1 ms to complete, while a single sweep of the moving mirror typically took 16 s to achieve a maximum possible resolution of $\sim 0.25 \text{ cm}^{-1}$. The operation of this interferometer in a time-resolved fashion relied on achieving synchronization between the external event and the mirror scan of the interferometer. In this implementation this was accomplished by using the HeNe reference laser signal, monitoring the position of the moving mirror of the interferometer, to trigger both the external event and the digitization of the associated transient signal.

For the case where the transient decays completely and may be repeated between successive mirror positions, this "continuous scan" method, employed for the experiments of thesis, is particularly simple. In the experiments of this thesis, the HeNe reference laser signal was used to trigger both the excitation event and a number of digitizations at fixed time delays with respect to the external event. This represents a large increase in data collection efficiency. The time required to completely record a single set of time-resolved interferograms is still short compared to the step-and-stop method⁹⁴, so that the acquisition of successive interferograms now smooth out the

effects of any long term variations affecting the transient. A portion of the IR emission spectrum arising from the $O(^1D) + HCl$ reaction is presented in figure 21, which displays spectra taken at time delays separated by $40\ \mu s$ and spanning a range of -20 to $540\ \mu s$ with respect to the initiation of the reaction. The quickly decreasing spectral lines in figure 21 originated from rotational levels of $OH(v=4)$, while the lines increasing in intensity arose from $HCl(v=1)$ rotational levels. The differing temporal behavior served to distinguish primary and secondary reactions: $HCl(v=1)$ was a product of a secondary reaction.

An additional complication may be presented by the maximum repetition rate of the transient. For example, even at the low mirror speed used in these experiments, the desired bandwidth of $3950\ cm^{-1}$ resulted in a $1\ ms$ time between successive mirror positions; however, the minimum time between transients was $3\ ms$ — a limitation in the maximum repetition rate of the transient. This required that the complete interferogram be built up from three successive scans. In each of the three scans every third point was recorded, but data recorded in subsequent scans was offset by one mirror position from the previous scan. The sorting process entailed in the reconstruction of the complete interferogram is illustrated in figure 22. Here (a), (b) and (c) represent three successive interferograms, with the excitation occurring at every third mirror position for each transient. The sorted interferogram for the first time delay is represented in (d).

(3.2) Specifics of the Time-resolved Accessory

The time-resolved aspect of the FTIR was accomplished using a commercial Nicolet 7199 interferometer and Nicolet 1180 computer, together with specialized hardware and software contained in two separate computer systems. Since PDP 11/83+

Figure 21: Complete set of time delayed emission spectra. Only the spectral region $2750\text{-}3000\text{ cm}^{-1}$ is shown, and displays P branch emissions from $\text{HCl}(v=1;J)$ states which increase with time and P branch emissions from $\text{OH}(v=4;J)$ states which decrease very quickly. The R branch of HCl is evident as the set of smaller peaks which persist in the OH spectral region. The time delays span from $-20\text{ }\mu\text{s}$ to $540\text{ }\mu\text{s}$ with respect to the excitation pulse which initiates the reaction.

Figure 22: Sorting method used to separate time delayed interferograms. (a), (b) and (c) represent data taken from three consecutive interferometer scans. During each ramp, representing the excitation event, three time delays are sampled. (d) shows the sorting process required to reconstruct a single, complete interferogram at the first time delay.

and 11/23 computers were used, these separate computers will be referred to henceforth simply as the 11/83 or the 11/23. In addition to the data collection taking place in the Nicolet in such a way as to provide one time delayed spectrum, the 11/83 provided a complete set of time delayed spectra. The timing for the time delays was set in a hardware interface external to 11/83 and required as input only two digital signals from the interferometer: the first of these was a TTL voltage signaling proper, forward scanning motion of the interferometer mirror (TKDA, "TaKe DAta"); the second was the appropriately divided TTL pulse train related to zero crossings of the signal generated by the HeNe reference laser (SCLK, "System CLock"). The SCLK period was an integer multiple of the period of the reference laser signal and provided an indication of the optical retardation. All the external timing signals had a fixed relationship to SCLK and thus, because of the constant mirror velocity, also had a fixed relationship to the optical path length difference. The only remaining signal coming from the interferometer was the amplified, analog, detector signal, appropriately bandpassed and modified to fit the complete voltage range of the A/D controlled by the 11/83.

The 11/23 was used to provide initial control over the SCLK signal from the interferometer and its primary functions were to output a timing pulse fixed in phase with respect to SCLK and to enable the creation of the transient event after having recorded the ZPD region. The aforementioned timing pulses output by the 11/23 would, under normal scanning conditions, initiate two related timing signals. One of these was a comb of pulses which triggered both a series of A/D conversions and the readout of the results by the 11/83. The second signal was used to trigger the laser. The laser trigger was set to occur between the first and second A/D trigger, so that the first spectrum obtained was the background signal. Typically, the background spectrum and the first product spectrum were at $-20\ \mu\text{s}$ and $20\ \mu\text{s}$ time delays with respect to the laser trigger.

The 11/83 controlled an 8-bit, 100 Mhz transient recorder (LeCroy, model 8818) which was used for the digitization of the analog interferometer signal; however, the transient recorder was only used in its "single sample" mode controlled by an external trigger. Ideally, one would capture the transient independently of the computer and read the results after a series of closely spaced digitizations occurred. Instead, the digitizer's "A/D Done" flag, set after each digitization in single sample mode, was polled in a carefully controlled software loop. The minimum time between successive digitizations in this single sample mode was under 20 μ s. An interdigitization spacing of 40 μ s was typically used to provide a series of about 15 spectra covering the entire duration of the transient signal (roughly 0.5 ms at the pressures and pumping speed used).

"Start-of-scan" and "end-of-scan" conditions were flagged to the 11/83 software either by continuously monitoring individual input lines or by using the interrupt lines of the parallel port. Also, most timing measurements for software debugging and performance measurements were provided by inserting single instructions, to initiate transitions on specific output lines, into the assembler code and viewing these output lines on an oscilloscope as the program executed. A slower A/D was used to measure the laser power. Every transient was corrected by scaling by a constant factor and dividing by the laser power of its corresponding laser pulse. An increase of 2-3 in signal to noise was provided by correcting for the laser power in this fashion, depending on how erratically the laser was running. A variation in laser power from pulse to pulse of 5-10% was usual.

The 11/83 had 4 Mbytes of memory, addressable using the extended addressing scheme of this series of computers. Since speed was crucial, the memory management unit of the 11/83 processor was controlled by directly accessing its control registers whenever required. Subroutines accomplishing this task were written for the less critical postprocessing requirements. Mass storage was provided by a Data Systems Design

DSD880 20 Mbyte hard disk and 8" floppy drive, and by a Condor-86 hard disk. General principles concerning the software for any real-time system were followed⁹⁷. In particular, no calls to operating system routines or device drivers were allowed in critical portions of the collection routine. Here all required operating system and device control functions were duplicated by routines written to have guaranteed maximum execution times. Real-time display was provided by coding specialized assembly language routines to control and buffer output to either a VGT100 or a TEK4010/4014 graphics terminal.

(3.3) Overview of the Data Acquisition Software

The data acquisition software for the 11/83 was developed by the author. The main program consisted of a simple command interpreter. Some fifty separate commands were present, most involving "Set" and "Show" functions of various sorts, both for parameters governing the data acquisition and for parameters involved with displaying, plotting, modifying or transforming interferograms. The most critical routine was the data collection routine, which collected and coadded data into extended memory and updated a status block concerning the interferograms in extended memory. Separate routines allowed sections of an interferogram at a particular time delay to be displayed from extended memory. Other commands dealt with storing and retrieving the separate time-delayed interferograms on hard or floppy disks, or coadding complete sets of time-delayed interferograms or spectra. The Fourier transforms of the spectra were calculated using a customized version of the Fast Hartley Transform⁹⁸, a variation of the FFT algorithm. Even with optimized assembly language routines, the 11/83 took ~2 minutes to perform each 32k double-sided transform of the 16k interferograms. With many time delays in each set of coaddable (see above) interferograms, and many sets of coaddable interferograms for each experiment, the calculation of power spectra still took many

hours. Ideally, a high speed vector or array processor should be used to perform the tedious but routine Fourier transforms in this experiment.

The purpose of the collection routine was to read the data from the digitizer and coadd it into memory. Since the speed of the computer was one of the fundamental limits, all routines executed during this phase were coded in PDP-11 MACRO assembly language; furthermore, care had to be taken to disable all possible interrupt routines from executing, since this would disrupt critical software timing loops. The highest priority interrupts were allowed to function only at well-defined stages during the data collection. As the 16-bit registers of the PDP-11 allow one to access only 64k of memory, the coaddition of data into the 4 megabytes of extended memory was accomplished by direct manipulation of the control registers of the memory management unit. Throughout the code, extensive use was made of registers to speed execution. As a rough rule, every fetch or store not within the instruction prefetch queue would add about 2-3 μ s to the execution time. The organization of the collection routine will presently be described.

The collection routine had two entry points. The first entry point corresponded to the 'RES' (RESume) instruction and its function was to continue data collection with the controlling parameters and extended memory left unchanged, whereas the second entry point corresponded to the 'COL' (COLlect) instruction, which reset all control parameters and memory pointers and zeroed the memory into which data would be coadded. Both entry points then executed a common section of initialization code: various control variables were initialized, the transient recorder parameters were set, and the parameters of the A/D which digitized the laser power were set. Then interrupts were disabled and a polling loop was entered to read a single digitized value of the detector signal upon the detection of a signal indicating the completion of the digitization of a single time delayed data point. Once the proper number of digitizations were accrued

into a buffer area for a single excitation event, code execution was continued at one of several code sections, depending on the interferogram point number.

The first interferogram point enabled an interrupt which caused the execution of an appropriate section of code when the end-of-scan condition was detected. The time delayed data points for this first interferogram position, as well as subsequent ones during this first phase of data acquisition, were simply stored in a buffer area of extended memory. After a preset number of data points, this phase continued storing data into the buffer while the maximum value of the interferogram within a specified window was located. The maximum which was found was then taken to be the zero path difference (ZPD). This calculation was spread over several interferogram points for reasons of timing. The data point number of the zero path difference often showed a slight drift throughout the course of an experiment.

During the next phase, the transient events began being created by the 11/23; simultaneously, the 11/83 program switched, from the straightforward storage of newly recorded data into the buffer area, to the preliminary division of such data by the laser power of the pulse which initiated that transient.

In the subsequent phase, after calculating various required parameters, the coaddition of excitation events, scaled and divided as before by the digitized power of the laser pulse, into a scan storage area (SSA) of extended memory was initiated. Concurrently, data previously stored into the buffer area was coadded into the ZPD region of the SSA using a distributed computing algorithm. While storing or coadding each interferogram into the SSA, corrections were made to account for any possible drift of the (previously calculated) ZPD location.

By the last phase, the ZPD region had been coadded completely, and coadding was continued into the SSA while checking that the number of data points collected did not overrun the allotted length of the SSA.

In this implementation, three SSAs were required since the maximum laser repetition rate was a third of the interferogram point frequency. Thus each of the three SSAs held data originating from every third interferogram point, but corresponding to a separate interferogram point modulo 3. The operation of these SSAs was dependent on synchronization being maintained between the 11/83 collection routine and the laser triggering routine of the 11/23 computer.

Atop this basic structure, several minor tasks were coordinated by the collection routine. The program had to keep track of when to turn the laser triggers on, and during the main part of the scan (interferogram points $> \sim 1000$) had to record the digitized laser power. Most of these secondary functions also had some degree of bookkeeping requirements in order to maintain a valid status block for each SSA. For reasons of speed as well as conserving memory, all data were kept as 16-bit integers.

The transient recorder data, however, displayed a large range of offsets, which in earlier versions of the program tended to overflow the data past the +32k limit and into the -32k range after approximately 60-70 coadditions for the time delay immediately following the excitation. This was corrected for by instituting an efficient algorithm which maintained a circular buffer containing up to 20 of the previous excitation events and the running average of those events. The calculation of the running average would be initiated during each scan at the point the laser trigger was enabled, and the value so obtained was used to remove any very low-frequency offsets from the incoming data. The cumulative average offset removed was stored in the status block of each SSA.

It was also necessary to poll the keyboard occasionally to allow either termination of the data collection at the end of the current interferometer stroke or an immediate abort of the collection routine. When the data collection was terminated from the keyboard, interrupt and trap vectors had to be restored to provide a successful return to the command processing environment. Related to the termination of scanning from the

keyboard was the end-of-scan signal. Depending on which interferogram point was being collected (i.e. which phase of the 11/83 collection routine was being executed) scans were classified as: "successfully aborted", if coadding had only taken place into buffer areas of extended memory; "successful", if a certain minimum number of data points had been collected; or "unsuccessful", if coadding into the SSA had begun but was not yet finished.

(3.4) General Experimental Aspects

This thesis involves measurements of the time-resolved infrared chemiluminescence in the $2000\text{--}3950\text{ cm}^{-1}$ wavelength region. In this region are the vibrational transitions of OH, HCl and HBr. With the spectral resolution of 1 cm^{-1} which was obtained, vibrational and rotational lines were fully resolved for P and R branches. The spin doublets of OH were resolved, but the Λ doublets were not. The analyzed spectra yielded relative populations of each rovibrational level as functions of time. Summing the rotational populations within each vibrational level yielded the vibrational distribution as a function of time. Of particular importance was the initial vibrational distribution of the $\text{OH}(^2\Pi; v, J)$. The time-resolved sequence of spectra provided a good estimate of this distribution and also elucidated secondary processes producing or consuming the observed species (see figure 21). Such secondary processes may be important in interpretations of earlier data with poorer or no time resolution.

The $\text{O}(^1\text{D}) + \text{RH}$ reactions were initiated by photolyzing ozone at a wavelength of 248 nm in a low pressure reaction chamber. The reaction chamber was a 30 cm high stainless steel cylinder of 25 cm internal diameter, fitted with 8 customized ports supporting windows, mirror mounts and pressure transducers as required. A top view of

the reaction vessel is shown schematically in figure 23. In figure 24, a side view representing elements inside the reaction vessel is shown.

The photolysis was accomplished by a Lumonics TE-860-4 KrF excimer laser which was fitted with high repetition rate electrodes and produced ~7 Watts of power when run at 330 Hz. The duration of the photolysis pulse was roughly 5 ns. To improve the photolysis efficiency, the unfocussed excimer beam made four passes of the reaction chamber, exiting along its incoming path. This multipass arrangement was achieved with two adjustable dielectric mirrors coated for maximum reflectivity at 248 nm and located inside the reaction chamber. The excimer beam entered the chamber through a Suprasil window. It was estimated that the $\sim 1 \times 4$ cm photolysis beam dissociated $(30 \pm 5)\%$ of the O_3 in its path

The reagents, O_3 and RH, were introduced and mixed 2-3 mm above the photolysis region through concentric glass tubes whose open ends were at the same height. Ozone flowed through the outer tube while the RH reactant was introduced through the central tube. Mixing was ensured by a small Teflon deflector plate suspended horizontally 2 mm below the inner tube.

The chemiluminescence was collected by a Welsh cell formed by four concave mirrors located in pairs on opposing interior walls of the reaction chamber. This formed a rectangular observation zone perpendicular to the photolysis region. The mirrors were gold coated for maximal reflectivity in the IR region. The collected emission exited the reaction chamber through an f/1 CaF_2 lens and entered the interferometer. The interferometer was aligned with this emission by detecting a small heat source located beyond the Welsh cell prior to each day's experiment. Following this, the mirrors forming the Welsh cell were adjusted for maximal collection efficiency by using a white light source temporarily placed at the interferometer entrance to create the appropriate

Figure 23: Top view of reaction chamber. Only major components are shown. This figure is not to scale.

Figure 24: Side view of interior of reaction chamber. Only major components are shown. This figure is not to scale. In experiments the adjustable gas inlets were positioned at the top of the photolysis beam. The photolysis beam crosses the top of the Welsh cell.

sequence of images on the mirrors when viewed by eye through the Welsh cell. Final minor adjustments of the Welsh cell were made by maximizing the experimental signal.

Ozone for these experiments was produced by slowly flowing O_2 at atmospheric pressure through a 15 kV AC discharge. The small fraction of ozone generated was preferentially adsorbed in a large silica gel trap at $\sim -80^\circ C$. The temperature of the coils and the discharge was controlled by surrounding them with methanol cooled by either making a dry ice slush or by an external refrigeration unit. Before each use, the coils were isolated and the O_2 was pumped away. Purity of the remaining ozone was ensured by performing the final pumping through the reaction chamber with all valves on the silica gel trap opened and obtaining a pressure of 0.5-1 Torr in the reaction vessel. As the purity of the ozone by this stage was already high, the pumping speed was reduced to prevent ozone explosions in the pumps. The flow of ozone was then throttled by manually controlling the six valves on the ozone trap, as well as the temperature and level of the surrounding methanol, to obtain the desired partial pressure of ozone in the reaction chamber.

Controlling the flow of the RH reactant was less problematic. The flow was set to yield the desired partial pressure and kept constant by ensuring that the backing pressure, controlled by a needle valve, and the ball reading in a flow tube on the inlet line were kept constant. The RH partial pressure was checked at least at the beginning and end of each set of scans (typically about two hours). During the experiment, ozone was added and controlled to keep the total pressure in the reaction chamber constant within ± 1 mTorr, as measured by an MKS Systems Model 227A pressure transducer. Typical partial pressures were 10 mTorr each of ozone and RH reagent. The reagents used were research grade gases from the Matheson Co. with stated purities for O_2 , HCl, HBr, H_2S and CH_4 of 99.8%, 99.0%, 99.8%, 99.0% and 99.99% respectively.

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MICRO

The reaction chamber was evacuated through a 30 cm gate valve situated atop a 38 cm diameter cryobaffle. The pumping was provided by a Varian VHS 400 15" diameter diffusion pump backed either by a 50 cfm Welch mechanical pump or by an Edwards EH500 Roots blower and E2M40 mechanical pump. The pumping speed was throttled by only partially opening the gate valve to obtain a pumping speed around 400 L/s. This pumping speed was sufficient to replace the contents of the reaction chamber between laser shots. To minimize contamination of the observation zone by products of wall collisions and to provide a cooler background around the Welsh Cell, four copper vanes suspended from a reservoir above the photolysis region were cooled by passing methanol through the reservoir. The methanol coolant for this reservoir and for the cryobaffle was maintained at $\sim -70^{\circ}\text{C}$ by recirculating it through a dry ice/methanol slush.

The interferometer was a Nicolet model 7199 controlled by a Nicolet 1180 computer. The interferometer contained the infrared detector and preamplifier, low- and high-pass filters, several variable gain amplifiers and an analog to digital converter as well as electronics controlling and stabilizing the mirror motion and coordinating its movement with the data acquisition process. A 1 mm^2 InSb infrared detector from Judsen Infrared was maintained at 77 K with liquid N_2 and fitted with a home-built, low noise, high gain preamplifier. Interferograms were collected under conditions of constant background temperature and total reactant pressure. Each experiment typically involved the coaddition of 500-2000 scans. Data was collected in increments of ~ 300 scans, each increment requiring about 2 hours as dictated by the life of the KrF gas mixture of the excimer laser.

(3.5) Analysis of the Spectra

The spectra were obtained by removing any offset present in the interferograms, zeroing interferogram points taken before the laser began firing, and performing a power transform using the Fast Hartley algorithm⁹⁸. Before analysis, the raw spectra were normalized by dividing by an experimentally determined reference spectrum representing the sensitivity of the interferometer and detector. This reference spectrum was obtained by measurements of a standard black body source.

The height of each spectral line in the normalized spectrum was divided by the A-factor of that transition to provide a relative measure of the population in the upper rovibrational state corresponding to that emission frequency. Error estimates were made by accounting for the noise present in the baseline of the spectra. A-factors for OH($X^2\Pi$) were obtained from calculations of Langhoff, Werner and Rosmus⁹⁹ and line positions were taken from a spectral compilation provided by the Air Force Geophysics Laboratories¹⁰⁰; for HCl($1\Sigma^+$), A-factors were obtained from transition moments calculated by Oba et al.¹⁰¹ using the dipole moment function of Ogilvie and Tipping¹⁰², and line positions were from term value expansions¹⁰³. Systematic errors resulting from the A-factors used were ignored. The program included provisions for deconvoluting overlapped lines, although this was an infrequent occurrence at the $\sim 1\text{ cm}^{-1}$ instrumental resolution obtained. The final rovibrational states to be analyzed were determined manually by instructing the analysis program to include only rotational levels which displayed signal-to-noise ratios greater than one.

P, Q and R branches were present, corresponding to $(J_{\text{upper}} - J_{\text{lower}}) = -1, 0$ and $+1$, for each of the spin states of OH. The $+$ and $-$ A doublets were degenerate within the resolution of the spectra. Q branches overlapped significantly and were not used. Reported populations are for the P branches of the $2\Pi_{3/2}$ state, since these were the

largest lines in the spectrum. The signal-to-noise ratio in the P branch of the $^2\Pi_{1/2}$ state was much poorer, but yielded populations close to half those of the $^2\Pi_{3/2}$ state, as expected statistically. A-factors for the R branch transitions were smaller than those for the P branch transitions.

Within the P branch, the A-factors increased with increasing J. It was thus not for reasons of poor transition probabilities that earlier chemiluminescence studies noted no highly rotationally excited products in the OH($v \geq 1$) populations — higher rotational states, hypothesized by some⁵⁶ to be possibly metastable, should be more easily detected than the partially relaxed distributions reported previously and presently.

Vibrational distributions were obtained by summing the populations of all rotational levels within each vibrational level. Since all time delays were recorded concurrently, the same scaling factor for absolute populations exists at each time delay. While this scaling factor is unknown, the relative populations, from one time delay to another, are still correct. This differs from previous implementations of time-resolved FTS, in which relative populations were only significant within each of the separately collected time-resolved interferograms.

After the completion of these analyses, it was found that a systematic error had been made throughout the analysis: instead of dividing the spectrum normalized by the detector sensitivity by the A-factor, an additional division by the energy per photon should have been performed. Over the small spectral ranges involved in these analyses, this was estimated to have resulted in a systematic error of ~5%, overestimating the population of higher v levels, and also higher J levels within each v level.

CHAPTER 4

(4.1) Introduction: $O(^1D) + HCl$

The reaction of $O(^1D_2)$ with HCl ,

has been the subject of several experimental investigations. Early observations⁷⁰ of the partially relaxed OH product detected vibrational levels up to $v = 2$. Later measurements¹⁰⁴ of the overall rate constant yielded a value for the rate constant k_1 of $(1.4 \pm 0.4) \times 10^{-10} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ over the temperature range¹⁰⁵ 200-350 K.

Reaction (1b), producing $H + ClO$, was postulated to be only a minor product channel in these latter studies. This conclusion was based on the weakness of the emission arising from the secondary reaction, $H + O_3 \rightarrow OH(v \leq 9) + O_2$. This secondary reaction occurs only when H atoms are formed in reaction (1b) and has a rate constant¹⁰⁶ of $\sim 1.5 \times 10^{-10} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$. This reaction produces $OH(v \leq 9)$ which emits around 630 nm via the $\Delta v = -6$ transitions of the Meinel band of OH . The transition rates within the Meinel band have A -factors of¹⁰⁶ $\sim 0.006 \text{ s}^{-1}$ (cf. $\sim 12 \text{ s}^{-1}$ for infrared $\Delta v = -1$ transitions). Another study¹⁰⁷ concluded that the UV absorption of ClO which was observed was due to the secondary reaction of Cl with O_3 instead of the $O(^1D) + HCl$ reaction. Ethane reacts very quickly with Cl to form HCl and C_2H_5 . When ethane was added the ClO absorption fell below the detection limit of this study. The ClO absorption which had been seen prior to the addition of ethane was construed to have been produced by a reaction of Cl and not by the direct mechanism of reaction (1b).

Furthermore, this study observed no ClO absorption when N_2O was used as a source for $\text{O}(^1\text{D})$, implying that O_3 was also likely to be involved in the measured ClO absorption. The minor nature of reaction (1b) was expected in this study, since this reaction channel is only slightly exothermic.

However, a recent investigation by Wine et al.¹⁰⁸ of reaction (1) included a detailed study of the branching ratios. They found that $(24 \pm 5)\%$ of reaction (1) produced $\text{H} + \text{ClO}$. This value was based on direct measurements of $\text{H}(^2\text{S})$ primary reaction product by resonance fluorescence detection in which the maximum absorption under conditions where HX ($\text{X} = \text{Cl}, \text{Br}$) dominated the $\text{O}(^1\text{D})$ removal was compared to the absorption signal obtained when HX was replaced with H_2 . The $\text{O}(^1\text{D}) + \text{H}_2$ reaction served to calibrate the yield, since this reaction had a previously determined yield¹⁰⁹ of $(98 \pm 2)\%$ for $\text{H}(^2\text{S})$. They also measured the total rate constant to be $k_1 = (1.50 \pm 0.18) \times 10^{-10} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ by measuring the appearance rate of $\text{O}(^3\text{P})$ as a function of $[\text{HX}]$. A more detailed kinetic analysis allowed the extraction of the branching ratio for reactions (1c) and the analogous $\text{O}(^1\text{D})$ quenching channel of the $\text{O}(^1\text{D}) + \text{HBr}$ reaction. This branching ratio was also determined by comparison of the signal to that obtained in the $\text{O}(^1\text{D}) + \text{N}_2$ reaction, which is known to produce $\text{O}(^3\text{P})$ with unit yield. The two methods of determining the branching ratio for the quenching channel agreed within their error estimates (e.g. $(7 \pm 5)\%$ for the former method and $(10 \pm 4)\%$ for the latter method for the branching ratio for reaction (1c)). Use of a weighted average of the branching ratios determined for reaction (1c) led to an estimate of a complete set of branching ratios for reactions (1a-c) of $(67 \pm 10)\%$, $(24 \pm 5)\%$ and $(9 \pm 5)\%$ respectively. This experimental and analytical procedure was also used for their analysis of the $\text{O}(^1\text{D}) + \text{HBr}$ reaction and their results for this reaction will be presented in the following chapter.

The internal state distribution of the OH product from reaction (1a) was investigated by Luntz¹¹⁰ in LIF studies. These studies were undertaken with experimental conditions (P_{O_3} , P_{HCl} , P_{Ar}) = $\sim(1, 10, 2000)$ mTorr) and procedures (time delay = 0.5 μ s) identical to those used in his earlier studies^{82,84} of H_2 and alkanes. A large rotational excitation was observed in the OH($v=0$) and OH($v=1$) products and both Λ doublets were observed to be equally populated. The ratio of OH($v=1$) / OH($v=0$) was estimated to be 1.5, based on "the vertical displacement of the [rotational] surprisal plots in the linear regime." This is presumed to have been calculated according to the Bernstein-Levine theory of branching ratios¹¹¹, which has been found to agree with experimentally observed branching ratios for the F + HD reaction¹¹². The rotational distribution of OH($v=0$) peaked sharply for $J \geq 20$, and was more inverted than predicted by phase space theory or RRHO (rigid rotor, harmonic oscillator) statistical models. Luntz concluded that the HOCl intermediate fragmented before the energy was equipartitioned among all possible modes.

Similar rotational inversions have been observed for the low-lying vibrational levels of the OH product of the O(¹D) + H_2 reaction. Recent Monte Carlo simulations of both the H_2 and HCl reactions by Holmlid et al.^{113,114} have demonstrated that such rotational inversions do not necessarily imply nonstatistical energy redistribution — the large rotational inversions can be a result of angular momentum constraints and are not necessarily a result of detailed potential energy surface features. Their approach was based on a random sampling of the initial impact parameter, relative velocity and internal molecular rotation to determine both the initial total energy and total angular momentum. In this approach, the internal distribution of the initially sampled total energy in complexes at the exit channel transition state geometry was random, as in the RRKM approach, with the additional restriction upon the microstates sampled at the transition state that the total angular momentum corresponding to this random sampling of initial

conditions also be conserved. This additional angular momentum constraint severely limited the available microstates available to the exit channel and considerably modified the rotational state distributions of the products from the near Boltzmann shape expected from standard RRKM models: the OH product was highly excited rotationally. The successful modelling of the rotational distributions in this approach was obtained only for certain choices of the location of the transition state and the height of the exit-channel barrier. The best agreement for the rotational distributions of the OH product of the $O(^1D) + H_2$ reaction was obtained for a transition state located outside the centrifugal barrier. This indicated that the uncoupling region for the rotational degree of freedom of the product molecule was outside the centrifugal barrier. Holmlid himself has recognized the failure of this method to simulate the inverted vibrational distributions. Such a failure of this method is not unexpected since the addition of an angular momentum constraint, being fundamentally concerned with the partitioning of rotational energy, would mainly be expected to modify rotational product distributions. Secondary effects are expected for translational degrees of freedom since restrictions on angular momentum also directly affect the allowed translational energies of the OH product.

The change in mass to HCl from H_2 only accentuated the rotational inversions Holmlid obtained. The effects of the angular momentum restriction upon the OH products of the (a) $O(^1D) + H_2$ and (b) $O(^1D) + HCl$ reactions are shown schematically in figure 25. This figure depicts typical angular momenta and illustrates implications of these angular momenta on the dynamics of the exit channel transition state. For clarity, the effects have been exaggerated. The total angular momentum, L_{tot} , is the result of orbital angular momentum (L_{orb}) of the atom about the center of mass of the diatomic molecule added vectorially to the rotational angular momentum (L_{rot}) of the diatom. Note that the (atom, diatom) pairs were ($O(^1D)$, HX) and (X, OH) for the entrance and product channels respectively, where X = H or Cl. When the mass is changed from X

Figure 25: Angular Momentum Conservation Effects in: (a) the $O(^1D) + H_2$ reaction and (b) the $O(^1D) + HCl$ reaction. Typical magnitudes and directions of the various angular momentum vectors are shown. All angular momentum vectors are in the plane of the figure, while v_H , v_{Cl} and v_{HCl} are perpendicular to the plane of the figure.

$= \text{H}$ to $\text{X} = \text{Cl}$, the reduced mass $\mu_{\text{O,HX}}$ increases from 1.8 to 11.1. Since for equivalent impact parameters and translational energies the orbital angular momentum scales as $\mu^{1/2}$, it is not surprising that the peak value of the L_{tot} distribution obtained by Holmlid increased from $\sim 0.9 \times 10^{-33}$ Js to $\sim 2.8 \times 10^{-33}$ Js. The increase in the value of L_{tot} is shown in figure 25. Because of the low reactant energies (in Holmlid's simulation $\langle E_T \rangle = 10^{-19}$ J for both $\text{O}(^1\text{D}) + \text{H}_2$ and $\text{O}(^1\text{D}) + \text{HCl}$), L_{tot} was relatively small; however, because of the large exothermicities, both these reactions had $L_{\text{orb;X,OH}} > L_{\text{tot}}$ in the product transition states. Obviously then, the angle made between the third angular momentum vector, $L_{\text{rot;OH}}$ of the product OH, and the orbital angular momentum of the products, $L_{\text{orb;X,OH}}$, had a maximum determined by a triangle rule. A purely microcanonical sampling of the transition state gave $L_{\text{rot}} \ll L_{\text{orb}}$ for most of the systems sampled. The effect of the additional requirement that L_{tot} be conserved was found to modify the sampling to favor values of $L_{\text{rot;OH}}$ which were higher, at the expense of $L_{\text{orb;X,OH}}$. This is the basis of the increased rotation in the OH product. The conservation of angular momentum in the product channel resulted in distributions of the angles α and β , the most probable values of which are shown schematically in figure 25. The increase in mass resulted in an increased angle α , on average, between the orbital and rotational angular momenta of the product channel as portrayed in the left half of the figure. The dynamical implications are illustrated in the right half of the figure, where angle α , L_{rot} and L_{tot} are in the plane of the paper, velocities v_{OH} and v_{X} are perpendicular to the plane of the paper and a circle representing the rotation of the OH product is in a plane perpendicular to L_{rot} . Recalling the discussion of A doubling effects, in which the singly occupied orbital was in the plane of rotation for Π^+ states in the limit of high rotational states of the product OH molecule, one sees from figure 25 that on average the broken R-O bond lies more in the plane of rotation of the exiting OH for the $\text{O}(^1\text{D}) + \text{H}_2$ reaction than for the $\text{O}(^1\text{D}) + \text{HCl}$ reaction. This is then a dynamical

reason which may explain Luntz's observation of Π^+ preference for the $O(^1D) + H_2$ reaction while no preference was seen for the $O(^1D) + HCl$ reaction. While it is conceivable that the change in α in Holmlid's simulation was a result of the changes (roughly doubling) in the potential constants describing the long-range exit channels of these two reactions, it seems more likely that these changes were caused by the larger mass of the Cl atom.

Connected with this discussion of the statistics, or lack thereof, is the observation of forward-backward symmetry of the OH scattering angle in molecular beam experiments⁷² of $O(^1D) + H_2$. Forward-backward symmetry in the center of mass frame of reference implies that either of the OH bonds breaks with equal probability in the HOH intermediate, and does not require that the intermediate be a "long-lived complex" with completely statistical energy disposal. Thus, even though it is likely that the high rotational inversion of the OH product in the $O(^1D)$ reactions with H_2 or HCl is strongly influenced by angular momentum constraints within an otherwise statistical exit channel, it is not necessary for this product energy to be equipartitioned among all possible modes. The energy disposal of the OH may still exhibit nonstatistical vibrational distributions.

One quasiclassical trajectory study¹¹⁵ of the $O(^1D) + HCl$ system has appeared, using an analytical fit to 633 *ab initio* data points¹¹⁶. As in the $O(^1D) + H_2$ surface, crossings with the triplet surface occur in the entrance channel region at extended HCl distances ($R_{HCl} \approx 2 \text{ \AA}$). Because the main interest of the study reported in reference 115 was low energy scattering, these intersections were not fit accurately. Difficulties in calculating the $O(^1D)$ - $O(^3P)$ splitting and inaccurate dissociation energies for the diatomics caused the exoergicity of the $OH + Cl$ product channel to be excessive. This was corrected by lowering the entrance channel by 40 kJ/mol in the fitted surface; however, the $H + ClO$ channel then became endothermic by 32 kJ/mol, rather than exothermic by 25 kJ/mol as it ought to have been. The resulting surface showed no

barrier to insertion, and barriers of ~ 9.2 and 96 kJ/mol for the collinear O-H-Cl and O-Cl-H approaches respectively. The resulting surface was necessarily exceedingly asymmetric with respect to $O(^1D)$ approaches to H or Cl. The potential minimum of the HOCl surface was at $R_{HO} = 0.99$ Å, $R_{OCl} = 1.83$ Å and an HOCl bond angle of 98.3° compared with the accepted structure¹¹⁷, based on microwave data, of $R_{HO} = 0.96$ Å, $R_{OCl} = 1.69$ Å and an HOCl bond angle of 102.5° .

In trajectory calculations on this HOCl surface, highly inverted rotational distributions in the lower vibrational levels were noted, peaking in $J \approx 28$ for $OH(v=0)$. For energy conservation reasons the rotational distributions were peaked at lower J and became broader in higher vibrational states of the product OH. The OH vibrational distribution itself was mildly inverted, peaking in $v = 2$ and 3 .

The dynamics displayed by these trajectories were compared to the $O(^1D) + H_2$ case¹¹⁸. For $O(^1D) + H_2$, the cross section as a function of impact parameter was roughly unity for all trajectories able to surmount the centrifugal barrier (impact parameters ≤ 2.3 Å). For $O(^1D) + HCl$, the reaction probability was between 0.6 and 0.8 for impact parameters below ~ 2.6 Å and fell to zero around 3.3 Å. The lower reaction probability at low impact parameters resulted from the presence of the high collinear barrier on the OClH surface, while the nonzero reaction probability at larger impact parameters resulted from the slightly more attractive long range potential for HOCl. To probe whether the vibrational and rotational distributions were a result of differences in the potential energy features or a result of the large change in mass from H to Cl, trajectories were run on the $O(^1D) + HCl$ surface with the Cl mass replaced by the H mass. It was found that the mass-substituted trajectories yielded only slightly more inverted vibrational distributions, which were much different from trajectories on the $O(^1D) + H_2$ surface. It was concluded that the inverted vibrational distribution was mainly a result of potential energy surface features rather than of the mass difference.

The mass-substituted HOCl surface yielded rotational distributions similar to the HOH results; thus the higher peaking of the OH rotational distribution for the $O(^1D) + HCl$ reaction was concluded to be primarily a mass effect (in agreement with the aforementioned results of Holmlid's analysis of angular momentum constraints). The angular distribution was slightly forward peaked, and this too was ascribed to a mass effect. In spite of the nonstatistical product distributions, the lifetime of the HOCl intermediate was long, about 0.5 ps, compared to ~0.05 ps for HOH. It was concluded by Schinke either that interactions between the various modes of the complex were weak, or that the vibrational inversion was largely an exit-channel effect (although what surface feature would be responsible for such an effect was not stated). However, it is also important to realize that the relative velocity of the reagents for the $O(^1D) + HCl$ reaction was roughly a quarter of the relative velocity in the $O(^1D) + H_2$ case because of the mass difference. Also, the Cl would take much longer to separate from the OH than the H would. These factors make it conceivable that dynamically similar motions occurred during the increased encounter time, with the increased lifetime of the complex being of little or no consequence for a more statistical product distribution.

One qualitative scheme, suggested by trajectory studies^{73,119} on the $O(^1D) + H_2$ p.e.s., for $O(^1D) + HX$ reactions involves insertion to form HOX in a highly excited level of the bending vibration. This insertion process itself could yield the highly rotationally excited distributions which have been measured for this type of reaction. The rapid initial increase in RHX as the $O(^1D)$ inserts results in excitation of the symmetric and antisymmetric vibrational modes of the intermediate, and can cause vibrational excitation of the product. These studies suggested that the attractiveness of the entrance (insertion) channel gives rise to a concomitant increase in vibrational excitation of the product OH.

The importance of long range orientation effects in the entrance channel was also demonstrated by Fitzcharles et al.¹²⁰ in their theoretical investigation of the isotope

effects in the $O(^1D) + HD$ reaction. This study investigated the OD/OH isotope ratios for reactions occurring on two potential energy surfaces with different long range behavior. The Murrell and Carter surface¹²¹ yielded an isotope ratio of 1.1 which was determined by the long range orientation towards collinear OHD or ODH geometries followed by the formation of a "loose" complex in which the $O(^1D)$ interacted predominantly with the first atom encountered, while the Schinke and Lester surface¹¹⁸ gave an isotope ratio of 1.8, determined to be a result of long range orientation effects favoring perpendicular insertion followed by the formation of a "tight" complex in which both OD and OH form strong bonds. The experimental OD/OH ratio is found to be 1.13 under thermal conditions¹²² and sufficient uncertainty was present in each of the surfaces to allow either mechanism to be plausible. The dynamical effects governing the isotope ratio both involved long range orientation effects, although the long range effects were very different for the two model surfaces. These mechanistic possibilities will be discussed in more detail in a later section of this chapter.

(4.2) Experimental

Two sets of spectra were obtained for the $O(^1D) + HCl$ reaction. The first set was taken at individual time delays of 50, 70, 150 and 200 μs at reagent pressures of 5 mTorr each of O_3 and HCl and formed the basis of a preliminary paper⁴³. This set of data was obtained using the preliminary version of the time-resolved FTS experiment, in which only the 11/23 and the Nicolet computers were required. This preliminary version yielded results at only one time delay for each experiment. The second set was recorded on the 11/83-based system. These spectra were taken at time delays from -20 to 540 μs in 40 μs increments and were done at partial pressures of 10 mTorr each of O_3 and HCl . All the reactions presented in this thesis used these reagent partial pressures, which

corresponded to a gas kinetic collision time of roughly 10 μ s. The final spectra are the results of 671 complete sets of time delayed interferograms (corresponding to over 2000 interferometer scans) taken over two days of experimenting.

(4.3) Results and Discussion

Samples of the raw spectra for the earlier results⁴³ and the more recent 11/83 data are displayed in figure 26. Considered on the basis of roughly equal numbers of gas kinetic collisions, both sets of spectra seemed quite similar: the vibrational distributions of at the earliest time delay of 50 μ s for the Nicolet (at half the reagent pressure of the 11/83 experiments) and 20 μ s for the 11/83 dataset agreed quite well. The complete set of spectra from the 11/83, however, offered a considerably more detailed time dependence (figure 21) and had individual spectra of better signal-to-noise ratio (SNR.)

Figure 27 displays the vibrational distributions of the OH product from the spectra of the modified data collection system. The error bars were based on a local estimate of the baseline noise only. For reference purposes, the raw data resulting from the population analysis is presented in table IX for the $O(^1D) + HCl$ reaction. This table shows the populations of rovibrational levels at each time delay. In this and all subsequent experiments, the spectrum at a time delay of -20 μ s displayed only a flat background and will henceforth be ignored. In many cases only the lowest 3-7 rotational levels were assigned. Should an appreciable number of higher rotational levels have been populated at levels too low to be detected, a systematic error would have resulted. Since $O(^1D)$ reactions populate the higher rotational states of low vibrational levels most strongly, the effect of such undetected rotational populations on the vibrational distribution would have been to weight the higher vibrational levels more highly. Such errors would have been most serious at the earliest time delays, should the rotational

Figure 26: Comparison of earliest spectra taken with the Nicolet and 11/83 computers. The upper spectrum was taken by the 11/83 data acquisition system after ~ 2 gas kinetic collisions, while the lower one was recorded by the Nicolet after ~ 2.5 gas kinetic collisions (at half the total pressure.)

Figure 27: Time dependent vibrational distribution of OH produced in the $O(^1D) + HCl$ reaction. In this figure, time increases towards the front of the figure. The vertical lines through each population are the error bars based on a local estimates of the baseline noise in the spectra.

**Table IX: Populations of Rovibrational Levels;
OH Product of the O(¹D) + HCl Reaction**

Time Delay (μ s)		Populations of J-levels of OH($X^2\Pi_{3/2}$) (arbitrary units) derived from P-branch lines								Total
		J=1	J=2	J=3	J=4	J=5	J=6	J=7	J=8	
20	v=1	16	28	12						55 $\pm$ 23
	v=2	67	59	40	30	13	30	9	5	254 $\pm$ 28
	v=3	156	150	115	71	40	13	11	6	562 $\pm$ 37
	v=4	138	136	91	44	26	16	5		457 $\pm$ 39
										$\Sigma = 1328 \pm 65$
60	v=1	33	28	18						79 $\pm$ 27
	v=2	120	97	59	42	15	37	7		377 $\pm$ 30
	v=3	170	166	112	67	34	7	4		561 $\pm$ 34
	v=4	100	97	63	31	14	5			311 $\pm$ 29
										$\Sigma = 1320 \pm 60$
100	v=1	47	38	21	10					116 $\pm$ 25
	v=2	114	101	60	38	9	26			348 $\pm$ 28
	v=3	143	135	90	53	27	6			454 $\pm$ 29
	v=4	71	67	40	18	7				202 $\pm$ 23
										$\Sigma = 1121 \pm 53$
140	v=1	56	52	28	11					147 $\pm$ 28
	v=2	116	101	58	36	10	24			346 $\pm$ 28
	v=3	116	110	73	37	22	5			364 $\pm$ 25
	v=4	53	39	26	12	5				135 $\pm$ 21
										$\Sigma = 991 \pm 51$
180	v=1	60	42	27	12					142 $\pm$ 27
	v=2	107	96	57	34	11	17			322 $\pm$ 26
	v=3	100	95	64	33	17				310 $\pm$ 22
	v=4	42	22	15	5					84 $\pm$ 20
										$\Sigma = 857 \pm 48$
220	v=1	53	44	22	10					129 $\pm$ 26
	v=2	111	91	57	32	7	16			314 $\pm$ 25
	v=3	85	80	50	23	14				251 $\pm$ 20
	v=4	17	11							29 $\pm$ 15
										$\Sigma = 722 \pm 44$
260	v=1	52	52	29	7					141 $\pm$ 29
	v=2	100	94	51	29	7	12			294 $\pm$ 23
	v=3	62	63	37	18	9				190 $\pm$ 17
										$\Sigma = 624 \pm 41$

300	v=1	51	46	26	16			139 ± 26
	v=2	90	84	44	26	8	6	258 ± 22
	v=3	54	47	30	18	9		157 ± 16
								$\Sigma = 554 \pm 38$
340	v=1	59	47	20	9			135 ± 26
	v=2	87	76	43	25	7	7	244 ± 20
	v=3	47	39	23	10	7		127 ± 13
								$\Sigma = 506 \pm 35$
380	v=1	70	48	23	14			155 ± 24
	v=2	78	74	40	20	6		218 ± 21
	v=3	31	26	15	11	6		89 ± 14
								$\Sigma = 462 \pm 35$
420	v=1	63	36	21	8			129 ± 25
	v=2	67	62	38	15	5		187 ± 18
	v=3	26	23	14	8	5		75 ± 13
								$\Sigma = 391 \pm 34$
460	v=1	44	36	25	10			116 ± 24
	v=2	63	56	36	16	6		177 ± 17
	v=3	26	14	15	6	6		67 ± 13
								$\Sigma = 360 \pm 32$
500	v=1	49	53	23	11			136 ± 23
	v=2	63	49	35	15	5		167 ± 16
	v=3	16	21	13	7	8		66 ± 11
								$\Sigma = 368 \pm 30$
540	v=1	44	42	19	7			112 ± 22
	v=2	59	49	29	15	5		157 ± 15
	v=3	17	13	10	6	6		52 ± 12
								$\Sigma = 320 \pm 30$

distribution within any vibrational level not have relaxed to place most population within the lowest ~3-8 rotational levels. As discussed in chapter 2, there was reason to expect the rotational distribution to have relaxed by the first time delay, since this time delay corresponded to 2 gas kinetic collisions and rotational relaxation typically occurs within a single gas kinetic collision time. Even if not relaxed, the IRCL technique is still capable of detecting substantial population of upper rotational levels, as demonstrated in a colleague's thesis by spectra of HF products in which populations up to $J \approx 26$ were readily detected⁶⁶.

The initial inverted vibrational distribution, peaking at OH($v=3$), was evident in figure 27, as well as its subsequent relaxation. Since all time delays had been recorded concurrently, the relative populations as functions of time were meaningful, and reflected both the pumping of the product out of the detection region and the relaxation of vibrationally excited OH by various energy transfer mechanisms. However, the total population at the second time delay was the same as at the first time delay. In later experiments, the population at the second time delay was substantially greater than at the first time delay, and possible reasons for this apparent anomaly will be discussed in later chapters.

The highest energetically allowed product, OH($v=4$), relaxed quickly, becoming undetectable after ~250 μ s. The OH($v=2$) and OH($v=3$) relaxed less quickly, since these levels were fed by relaxation from higher levels. The OH($v=1$) population actually increased for the first ~140 μ s, indicating that the feeding rate from upper levels was slightly greater than the combined effects of pumping and relaxation. The relative populations relaxed to peak in OH($v=2$) by 180 μ s, which remained the most populated level thereafter. The normalized initial distribution of OH was measured to be $P_{OH}(v=1:2:3:4) = (4 \pm 2): (19 \pm 2): (42 \pm 3): (34 \pm 3)$.

A sequence of some of the spectra used for the calculation of these distributions is shown in figure 28 (the spectra not shown simply continued the trends apparent in this figure). One notes that there were prompt HCl peaks, which grew in size with time in the lowest vibrational level ($2700\text{-}3000\text{ cm}^{-1}$). Detection of the HCl product was facilitated by the higher A-factors for these transitions as compared to the A-factors for OH. The raw results of the population analysis for the HCl product are presented in table X and the time dependence of the vibrational distribution is plotted in figure 29. The relative populations of the HCl and OH products of the $\text{O}(^1\text{D}) + \text{HCl}$ system, in figures 29 and 27 respectively, are also meaningful (note the change in direction of the time delay axis and the change in scale of the "population" axis). At the earliest time delay, the total population of $\text{HCl}^\dagger$ was $(8 \pm 1)\%$ of the total $\text{OH}^\dagger$ population. This was then a crude estimate of the branching ratio between reactions (1a) and (1c), for which the detailed investigation of Wine et al. obtained $(15 \pm 8)\%$. The estimate of $(8 \pm 1)\%$ was subject to large uncertainties. First, the product populations of $\text{OH}(v=0)$ and $\text{HCl}(v=0)$ were undetermined. Second, the $\text{HCl}(v=1)$ may have partly been produced in a secondary reaction, even at the earliest time delay (see below). Third, both HCl and OH may have had residual undetected rotational levels at the earliest time delay.

The normalized initial distribution of vibrationally excited HCl was measured to be $P_{\text{HCl}}(v=1:2:3:4:5) = (50 \pm 8): (12 \pm 4): (11 \pm 3): (18 \pm 3): (9 \pm 2)$. Since the HCl peaks were smaller than the OH peaks, the error estimates for the HCl distributions were larger. This distribution of HCl was bimodal, with a peak in $\text{HCl}(v=1)$ and a secondary maximum in $\text{HCl}(v=4)$. The analyzed HCl distributions, plotted in figure 29, show that this secondary maximum relaxed much as one would expect. The maximum accessible level for the nonreactive electronic quenching of $\text{O}(^1\text{D})$ to $\text{O}(^3\text{P})$, $\text{HCl}(v=5)$, disappeared between 100-140 μs . $\text{HCl}(v=4)$ peaked early, $\text{HCl}(v=3)$ peaked around

Figure 28: Samples of time delayed spectra for the $O(^1D) + HCl$ reaction. The frequency range spanned in these emission spectra is from 2300 to 3600 cm^{-1} . Not all time delays are present in this figure, intermediate spectra simply having continued the trends evident in the spectra presented in this figure.

300	v=1	8	17	16	24	25	33	28	26	15	4	198 ± 16
	v=2	1	6	6	8	6	2	2	2			34 ± 7
	v=3	1	2	4	3	3	2	2				16 ± 3
												$\Sigma = 249 \pm 17$
340	v=1	7	17	18	24	25	28	30	26	17	4	198 ± 14
	v=2	1	6	7	10	7	2	4				37 ± 6
	v=3	1	2	4	3	3	3					16 ± 3
												$\Sigma = 251 \pm 15$
380	v=1	8	16	18	25	29	30	30	28	18	4	205 ± 14
	v=2	1	5	4	8	6	2	2				27 ± 6
	v=3	0	2	4	2	3	2	2				15 ± 3
												$\Sigma = 247 \pm 16$
420	v=1	9	15	18	22	25	32	28	27	13	3	191 ± 14
	v=2	1	4	4	7	5	2	2				26 ± 5
	v=3	0	1	2	2	2	2					9 ± 3
												$\Sigma = 227 \pm 15$
460	v=1	9	17	18	22	27	26	32	25	19	4	197 ± 13
	v=2	1	4	4	7	4	2	2				24 ± 6
	v=3	0	0	1	2	2	1					6 ± 3
												$\Sigma = 228 \pm 15$
500	v=1	7	17	16	21	24	26	27	24	16	4	183 ± 14
	v=2	1	3	3	6	4	2	2				22 ± 6
	v=3	0	0	2	2	1	2					7 ± 3
												$\Sigma = 202 \pm 14$
540	v=1	8	14	19	20	23	26	28	24	14	4	180 ± 13
	v=2	1	3	3	6	3	2	2				20 ± 5
	v=3	0	0	2								2 ± 1
												$\Sigma = 213 \pm 16$

HCl Product from the $O(^1D_2) + HCl$ reaction

Figure 29: Time dependent vibrational distribution of HCl produced in the $O(^1D) + HCl$ reaction, as in figure 27. In this figure, time increases towards the back of the figure.

100-140 μs , and $\text{HCl}(v=2)$ peaked around 200-300 μs and relaxed more slowly than higher vibrational levels.

In contrast, the initial maximum in $\text{HCl}(v=1)$ increased rapidly for the first 300 μs . The usefulness of the time-resolved method in distinguishing primary and secondary processes is evident: the $\text{HCl}(v \geq 2)$ was the primary product of the $\text{O}({}^1\text{D}) + \text{HCl} \rightarrow \text{O}({}^3\text{P}) + \text{HCl}^\dagger$ electronic-to-vibrational (E-V) quenching channel, while the large population of $\text{HCl}(v=1)$ resulted mostly from a secondary process involving vibrational (V-V) energy transfer from the primary $\text{OH}^\dagger$ to the (unreacted) $\text{HCl}(v=0)$ reagent.

The persistence of $\text{HCl}(v=2)$ may indicate that V-V processes populated this level as well. This hypothesis was supported by the observation that, even with pumping depleting all levels equally, the total population of $\text{HCl}(v > 1)$ was seen to increase for the first ~ 200 μs . Two possibilities for the formation of $\text{HCl}(v=2)$ from lower vibrational levels are: (1) direct excitation of $\text{HCl}(v=0)$ reagent to $\text{HCl}(v=2)$ and (2) excitation of the secondary population of $\text{HCl}(v=1)$ to $\text{HCl}(v=2)$. Both these processes involve V-V energy transfer from excited $\text{OH}^\dagger$ molecules. The second process is expected to be of lesser importance, since the concentration of unreacted $\text{HCl}(v=0)$ reagent is at least three orders of magnitude higher than the concentration of $\text{HCl}(v=1)$.

More generally, one must consider V-V processes of the form

which are exothermic for $m \leq n$. Vibrational energy transfer rates are almost always greatest when the energy mismatch is small. On this basis one expects the largest V-V rates for the production of $\text{HCl}(v=1)$ to occur for energy transfer from $\text{OH}(v=4)$ to $\text{HCl}(v=0)$ since the spectral regions of emissions from $\text{OH}(v=4)$ and $\text{HCl}(v=1)$ are the most similar of all populated vibrational levels in this experiment. Interestingly, the prevalence of $\text{HCl}(v=1)$ in states with $J \approx 7-8$ (see table X), presumably produced directly from low rotational levels ($J \approx 2$) populated in the ground state HCl reagent by an energy

transfer mechanism involving $\Delta J = 6$ changes in rotational state, corresponds energetically with OH deexcitations from $v=1$ which change the OH rotational level by $\Delta J = \pm 1$. Specifically, the rotational distribution of HCl at the earliest time delay leads one to suggest that there exist a particularly efficient V-V mechanism populating $\text{HCl}(v=1; J=7-9)$ and that multiquantum rotational changes may be significant in any detailed modelling of these vibrotational energy transfers.

Figure 30 displays a correlation diagram for reaction (1). $\text{O}(^1\text{D}) + \text{HCl}$ correlates with the dominant $\text{OH}(^2\Pi)$ product channel. It is evident that crossings between the triplet and singlet surfaces must have been responsible for the large cross sections of the electronic quenching channel. The possible crossings occur on the steep entrance channel of the lowest singlet surface ($^1\text{A}'$), where the lowest triplet surface ($^3\text{A}''$) is crossed, and around the equilibrium HOCl geometry and exit channel in the first excited singlet ($^1\text{A}''$) and triplet ($^3\text{A}'$) states. The separation of the excited states around the equilibrium geometry has been calculated by *ab initio* CI techniques^{87,123} to be 18 kJ/mol, which was approximately the uncertainty in the calculation. Also displayed in figure 30 are the normalized vibrational energy distributions of the primary HCl and OH products. The darkened areas represent the error estimates in the distributions. The $\text{HCl}(v=1)$ peak from the secondary V-V process has arbitrarily been assigned a questionable value of 10% in this figure since the primary population of $\text{HCl}(v=1)$ was obscured by the secondary V-V energy transfer process. No estimates are given for products in the ground vibrational level.

The primary, vibrationally inverted distributions of HCl and OH were energetically similar. This suggested that both products may have originated from a similar region of the potential energy surface. Furthermore, the exit channel mass combinations and energy release were very similar for both these channels. These considerations suggested that the large cross sections for the spin-forbidden quenching

Figure 30: Correlation diagram and primary vibrational distributions for the $\text{O}(^1\text{D}) + \text{HCl}$ reaction. The curved arrows represent smooth changes from the equilibrium potentials to the collinear O-H-Cl surfaces. The vibrational distributions of excited HCl and OH products are shown at the left and the right hand sides of the figure, respectively. The filled in areas denote the error estimates for these vibrational populations.

channel may have arisen from crossings of the first excited triplet and singlet surfaces, and not from the crossings involving a much smaller range of nuclear configurations in the entrance channel of the lowest singlet surface.

Figure 30 also displays the energetics for the collinear O-HCl approach. In this $C_{\infty v}$ geometry, the $\tilde{X}^1A'$ ground state correlates with the $^1\Sigma^+$ state, the triplet states both correlate with the $^3\Pi$ state, and the first and second excited singlet states both correlate with the $^1\Pi$ state. As one changes the nuclear configuration between the equilibrium and $C_{\infty v}$ geometries the energy of each state changes smoothly between the energy at the equilibrium geometry and the energy in the $C_{\infty v}$ geometry. The energy of the $^3\Pi$ state has been taken to be close to the activation energy for the $O(^3P) + HCl$ reaction¹²⁴ of 25 kJ/mol. The energies of the $^1\Sigma^+$ and $^1\Pi$ states in figure 30 are not known, but very little barrier, if any, is expected for a collinear reaction occurring on the $^1\Pi$ surface. In any event, both of the excited singlet states and the lowest triplet states at the equilibrium geometry decrease in energy as one changes to end-on approaches. Towards collinear H-O-Cl geometries, the $^1A''$ energy increases and the $^3A'$ energy decreases. The net result is that these excited states remain in close proximity for a wide range of geometries. These first excited singlet and triplet states remain nearby for a range of geometries through which almost all of the reactive encounters will probably pass, so that the probability of a transfer from the initial, excited singlet surface to the excited triplet surface is heightened.

Recalling that the entrance channel crossings of the triplet states with the lowest singlet state occur far out in the entrance channel, one expects these crossings: (1) to be sharp, (2) to have a restricted range for which the singlet and triplet surfaces are close and (3) to occur at a geometry which will be traversed only once by any reactive trajectory. This leads one to posit that the ground state, entrance channel crossing of the ground $\tilde{X}^1A'$ state with either of the triplet states may be of lesser importance.

However, if the entrance channel singlet-triplet crossing had been of import the observed HCl vibrational distributions themselves would have been consistent with this possibility: because of the high reagent energies, if an $O(^1D)/HCl$ encounter should have availed itself of this entrance channel crossing, one would not expect products to have been formed immediately. Instead, one would still expect the encounter to have continued along the triplet manifold into the strong interaction region, preferably assuming a collinear O-H-Cl geometry and resulting in abstractive dynamics favoring high product vibration. Different considerations are required to successfully argue against the involvement of the ground state singlet-triplet crossing. Such arguments will be presented later.

Given the possible importance of these excited states, one might hope to have seen a bimodal distribution for the OH product as a result of two distinct reaction channels: one channel involves the ground $\tilde{X}^1A'$ state; the other, the excited $^1A''$ state. The ground state channel is not expected to yield $OH(v=0)$ exclusively, which would be undetected in this emission experiment. Schinke's trajectory calculations, which involved the ground state singlet surface only, indicated that a mild vibrational inversion was expected for this channel. The increased vibrational inversion present in our experimental results as compared to the trajectory calculation may partly have been a result of the involvement of the first excited singlet state in the dynamics. Also, quasiclassical trajectory calculations usually smooth out local variations in the vibrational distributions because of the wide binning procedure used to determine product vibrational distributions¹¹⁴. Since the first excited states of HOCl resulted from excitations from orbitals of π^* to σ^* character for the HO-Cl bond in the $C_{\infty v}$ H-O-Cl configuration⁸⁷, the exit channel of the excited $^1A''$ state was very repulsive, and was expected to yield vibrationally excited products. Furthermore, the excited $^1A''$ and $^3A''$ states are predisposed towards a collinear OH-Cl exit channel geometry, which could

have increased the fraction of energy deposited into OH vibration if these exit channel geometries were in fact reached. Thus the inverted OH vibrational distribution is expected to have been a result of both the repulsive exit channel dynamics favoring collinear Cl-H-O geometries on the first excited singlet (or triplet) state and the dynamics on the ground state potential energy surface. The inverted $\text{OH}^\dagger$ distribution which was measured is tentatively described as an effect of the long range orientation into a steeply sloped potential well favoring insertion geometries. Such an entrance channel results in vibrational excitation of the highly excited, transient HOCl complex. This vibrational excitation of the complex is converted into vibration of the $\text{OH}(^2\Pi)$ product.

One might expect^{125,126} the ground state, entrance channel surface crossings to influence the rate of the reaction

The activation energy for this reaction on the triplet surface is 25 ± 1 kJ/mol, less than the energy of an HCl vibrational quantum, $E_v \approx 35$ kJ/mol. The vibrational dependence of rate constants for this reaction has been studied experimentally by Butler et al.¹²⁷, who found that the vibrational enhancement of two orders of magnitude for each vibrational quantum of HCl was in accord with the reaction taking place entirely on the triplet surface, as predicted by quasiclassical trajectories on a LEPS potential energy surface for this reaction¹²⁸. For the reaction of $\text{O}(^3\text{P})$ with HCl, it was found that vibrational energy of the reactants was efficiently converted into vibrational energy of the products.

A similar vibrational adiabaticity has also been observed for the reverse reaction,

by Blackwell et al.¹²⁹. The lifetime of a complex formed during reaction (4) would be much longer than one formed by reaction (1) since much less potential energy would be released if the HOCl well were entered. It was concluded that reactive encounters did not

traverse the deep HOCl well, since for this reaction the entrance into the well would be expected to lead to formation of a long lived collision complex and statistical product distributions.

Since these $O(^3P)$ reactions, (3) and (4), would have traversed the ground state surface crossing region at lower velocity (and thus spend more time in the crossing region) than during the reaction with $O(^1D)$, one would have expected the effects of such surface crossings to be more pronounced. The failure to observe the effects of surface crossings in reactions (3) and (4) provided further evidence that the singlet-triplet conversion of the title reaction involved the first excited singlet and triplet states instead.

The unimportance of the singlet surface in reactions of $O(^3P)$ seems to be a general feature. Andresen and Luntz investigated reactions of $O(^3P)$ with neopentane $[C(CH_3)_4]$, cyclohexane $[C_6H_{12}]$ and isobutane $[(CH_3)_3CH]$ by both LIF⁸⁵ and quasiclassical trajectories on model LEPS surfaces¹³⁰. They interpreted the low rotational excitation of the product OH as a reflection of a collinear R-H-O exit channel and suggested that this also formed the dominant entrance channel approach as well. The rotational distribution was almost independent of the collisional energy, displaying only a very slight broadening as the collisional energy was increased from 20 to 30 kJ/mol. This was understood as an indication that the potential must rise steeply away from collinear configurations; otherwise, substantially more bent exit channel geometries would be available for more energetic collisions, and the torques on the exiting OH would result in much increased rotational energies at the expense of translation or vibration. Only for the most exothermic reactions, with tertiary hydrogens, was vibrational inversion noted, with $P_{OH}(v=1)/P_{OH}(v=0) = 1.4$ for the isobutane reaction. This tendency for more exothermic reactions on collinear surfaces to have earlier barriers (i.e. more "attractive" potential surfaces) which result in increased product vibration was corroborated in their trajectory simulations and had been suggested nearly two decades

ago to be a general occurrence¹³¹. Andresen and Luntz found no preference for either Λ doublet, as they expected for reactions populating low J levels, since low rotational states cannot be associated with directed orbitals. However they did observe a preference for the $\Pi_{3/2}$ spin state, which was populated about twice as heavily as was statistically expected. This was explained as a result of only partial collisional mixing having occurred among the closely spaced $^3\Pi_0$ and $^3\Pi_2$ manifolds originating from the $O(^3P_0)$ and $O(^3P_2)$ sublevels of the $O(^3P)$ ground state: the $^3\Pi_0$ manifold correlated with the $^2\Pi_{1/2}$ state of OH and the $^3\Pi_2$ manifold connected to the $^2\Pi_{3/2}$ state, while the $O(^3P_1)$ state correlated with a $^3\Sigma$ surface which did not correlate with $OH(^2\Pi)$. The model calculations involved a surface identical for all hydrocarbons except for known variations in bond strength. The three adjustable Sato parameters were determined solely by attempting to reproduce three of the experimental results for the reaction of $O(^3P)$ with a secondary RH: the vibrational ratio, $P_{OH(v=1)}/P_{OH(v=0)}$; the activation energy; and the rotational distribution of the $OH(v=0)$ product. "All other aspects of the experiments were correctly predicted by the model, including the variation in OH vibrational partitioning and reaction threshold with the type of RH bond abstracted. Thus excellent agreement is obtained between this model and all facets of the experimental results."¹³⁰ No mention was made of the ground state singlet-triplet crossing in this work.

(4.4) Mechanistic Hypotheses

The importance of long range orientation effects in the entrance channel was also demonstrated by Fitzcharles and Schatz¹²⁰ (FS) in their theoretical investigation of the isotope effects in the $O(^1D) + HD$ reaction. In this study, the OD/OH isotope ratios were determined for two potential surfaces. It was found that the Murrell and Carter (MC) surface¹²¹ yielded an isotope ratio of 1.1 which was determined by the long range

orientation towards collinear OHD or ODH geometries followed by the formation of a loose complex while the Schinke and Lester¹¹⁸ surface 1 (SL1) gave an isotope ratio of 1.8 as a result of long range orientation effects favoring perpendicular insertion, the formation of a tight complex in which both OD and OH formed strong bonds and the dissociation of this complex by a hard collision between H and D in which the lighter H atom usually exited with more energy. For comparison, the experimental OD/OH ratio was found to be 1.13 under thermal conditions¹²². The dynamical effects governing the isotope ratio both involved long range orientation effects, although the long range effects were very different for the two model surfaces. The MC surface favored collinear geometries while the SL1 surface had a collinear barrier to reaction. Trajectories were also run on the SL3 surface, which had no collinear barrier but still did not force the HD to orient to collinear geometries as in the MC surface, and it was found that the majority of reactive trajectories were still very similar to those run on the SL1 surface.

Since similar potential energy surfaces figure in discussions of $O(^1D) + HX$ reactions, a more detailed explanation of the various mechanisms proposed by FS for the $O(^1D) + HD$ reaction will now be given. FS defined the angle of approach, θ , as the angle between the O and D atoms about the center of mass of the HD at the first point in the trajectory at which either the OD or OH distance is equal to its equilibrium, diatomic value.

The MC surface was found to have angles of approach mostly within 30° of collinear. Trajectories with $\theta \approx 180^\circ$ ($O^H D$) approaches formed OH preferentially while $\theta \approx 0^\circ$ ($H D^O$) approaches tended to form OD. To investigate the dynamics of these collisions, they defined a vibrational action for both OH and OD throughout the existence of the complex. This vibrational action formed a relative measure of the vibrational excitation in each OH and OD bond throughout the course of the collision. In a typical $\theta \approx 0^\circ$ ($H D^O$) trajectory on the MC surface, they showed that the vibrational energy in the

OD remained small throughout the lifetime of the complex, while the vibrational excitation of OH remained much larger, briefly exceeding the diatomic dissociation limit twice during the lifetime of the complex. In general they proposed that on the MC surface the first bond formed eventually becomes the product: the second bond remains highly excited throughout the course of the collision and does not impart much of this energy to the first bond (i.e. a "loose" complex is formed). They suggested that the H atom in this complex could be thought of as loosely bound to the initially formed OD and that the H atom was "perhaps best described as orbiting about OD, passing through the collinear ODH valley ..." [at an intermediate stage of the complex]. Immediately prior to dissociating into H + OD, the OH bond was highly compressed and the complex of the sample trajectory was in a nearly collinear HOD geometry.

The approach angles on the SL1 surface ranged from ~ 40 - 160° . OD was formed at all approach angles, while OH was formed mainly for approach angles $> 100^\circ$. The sample trajectory presented by FS was for $\theta = 57^\circ$ and formed the OD product. The complex formed on the SL1 surface was shorter lived than on the MC surface. Low values for both OD and OH vibrational actions were quickly achieved and maintained during the lifetime of the complex. This indicated that both bonds in the complex were excited to roughly the same degree (i.e. a "tight" complex). This is what would be expected for more perpendicular approaches than occur on the MC surface. The presence of a collinear barrier on the SL1 surface caused the bending motion to be more constrained than on the previously discussed MC surface: no orbiting behavior of the H atom was seen on the SL1 surface. Immediately prior to dissociation a highly compressed complex was formed, with all three bond lengths very short. The H and D atoms underwent a hard collision during this period and the H atom was ejected. If the momenta imparted to the H and D atoms were the same in this hard collision, then the H atom would have about twice the velocity of the D atom and would be preferentially

ejected. FS point out that the relative energies imparted to H and D will depend on the relative phases of the OH and OD stretches. These phases are connected with the angle of approach (as defined by SF) and result in the calculated dependence of the branching ratio on the angle of approach θ .

Both the MC and SL1 reaction mechanisms adequately explained the rotational excitation of the products. The actual dynamics of the $O(^1D) + H_2$ reaction is still unclear, and was shown to be very sensitive to details of the long-range potential. Since even a description of the $O(^1D) + HD$ reaction presents such problems when one tries to explain the observed product energy distribution, it seems clear that one cannot expect to propose a single required mechanism for more complicated $O(^1D) + RH$ reactions, where the fine details of the long range interactions are even less well known. Nevertheless, one may try to imagine the more complicated reactions as generalizations of the proposed mechanisms for the $O(^1D) + H_2$ reactions.

One may consider the effects upon the previously suggested dynamical pictures of further increasing the mass of the R· partner from D to Cl. The potential energy surface is also changed, but for a simplistic initial picture, the change will be considered as simply a higher potential energy for the ClO product than for the OH product. In this case, the mass combination has been changed from H + LL (heavy + light-light) to H + LH. The H atom velocity is now much higher than that of either of its partners in the complex. Collisions of H with either O or Cl will not change the motion of these much heavier partners as much as it will change the H atom motion. For this reason, the dynamics will now be dominated by the ponderous collision of the two heavy atoms, with the H atom "spectator" adapting its motion to the potential energy surface to a greater extent.

Consider a nearly end-on $O \rightarrow \leftarrow ClH$ approach angle in a mechanism like that on the MC surface. The H will now be pulled counterclockwise around the OCl in response

to the potential well at the equilibrium HOCl geometry. Meanwhile, the O will collide with the Cl and exit to the right; Cl will exit left. Should the loosely orbiting H atom by this time be in a position resulting in an $\text{H} \leftarrow \text{ClO} \rightarrow$ geometry, the O and Cl will not separate as readily as they would have in the original (symmetric) MC mechanism because of the increased height of the ClO exit channel; rather, they will reverse their directions and come in for another ClO collision. Should the H atom after the first ClO collision result in a $\text{H} \leftarrow \text{OCl} \rightarrow$ geometry then the OH product will form. The O atom will be ejected more energetically than it would have in a corresponding $\text{H} \leftarrow \text{OD} \rightarrow$ geometry because of the high Cl mass. This would result in increased possibilities for product rotation and vibration. This mechanism is partially illustrated in figure 31(a). A similar mechanism may be imagined for the $\text{O} \rightarrow \leftarrow \text{HCl}$ approach.

For the SL1 mechanism involving a near perpendicular approach and a hard collision between H and Cl in a "tight" geometry of the complex, one may imagine the scenario in figure 31(b) to be typical. The oxygen inserts forming a ClOH geometry. The oxygen passes through the ClH and the H atom rotates around the ClO. The hydrogen eventually (possibly after more than one inversion through the collinear ClOH geometry) collides with the Cl and the hard collision reverses the direction of the H and modifies the Cl direction to a much lesser extent. This revised SL1 mechanism leads one to expect the H to carry off even more energy than it would have in a collision with the D atom and to result in even more rotationally excited product OH. It seems that a more sophisticated model of reactions involving near perpendicular approaches would be required to explain the effects of the mass substitution on the product vibrational energy. One possible variation is to hypothesize that the "hard collision" preceding dissociation involves the O and Cl atoms instead of the H and Cl atoms. The resultant exit channel is then similar to the MC case described above, in which there exists an increased

Figure 31: Illustrative MC and SL1 mechanisms. The major features of these two dynamical mechanisms are adapted here for the $O(^1D) + HCl$ reaction and shown in parts (a) and (b) of the figure, respectively.

possibility for vibrational or rotational excitation of the OH depending on what range of geometries the H is sampling while the O rebounds from the Cl.

Some experimental results for a number of related reactions will now be briefly discussed. Isotopic branching ratios for $A + HD$ reactions forming AD or AH have been studied for a variety of A atoms. Bersohn et al.¹²² reported experimental results for $A = F(^2P)$, $O(^1D)$ and $S(^1D)$. The $F(^2P) + HD$ reaction favored abstraction while the $O(^1D)$ and $S(^1D)$ reactions favored insertion. The abstraction reaction had a branching ratio FD/FH of 0.66 ± 0.10 . This was rationalized by observing that the HD reagent rotated with the H atom further from the center of mass than the D atom, so it was more probable that the F react with the H atom along collinear F-H-D geometries instead of F-D-H geometries. For $O(^1D)$ and $S(^1D)$ insertion reactions, Bersohn explained the AD/AH branching ratios of 1.13 ± 0.08 and 1.91 ± 0.10 by observing that in the HAD complex, with the same forces acting on H and D on average, the lighter H atom should have a higher probability of escaping.

The reactions of $Mg(3s3p^1P_1)$ with $H_2(D_2)$ forming $MgH(MgD) (X^2\Sigma^+)$ have been investigated by Umemoto and Breckenridge¹³². $Mg(^1P_1)$ was formed by irradiating a $Mg/He/H_2(D_2)$ vapor with a laser pulse at 285.2 nm. The $MgH(MgD)$ product was detected by LIF using the $A^2\Pi \leftarrow X^2\Sigma^+$ transitions. Spectral simulation techniques of the low resolution spectra obtained allowed the extraction of rotational populations for $MgH(v=0; J=0-30)$ and $MgH(v=1; J=0-20)$. The LIF probe delay was 5 ns, so the product was judged to have undergone little relaxation. This was checked by lengthening the time delay and increasing the He pressure until relaxation effects were noticeable. The product distributions displayed two distinct rotational components. The high J component was incompletely described by the available data, but extrapolating its population to higher rotational levels by assuming a linear surprisal resulted in an estimate that ~90% of the reaction produced high rotational excitation in the $MgH(MgD)$

product. The high J component was explained by a side-on insertion of $\text{Mg}(^1\text{P}_1)$ into the H_2 molecule: calculations and qualitative considerations showed that this insertion channel would be attractive. The low J component was suggested to have arisen from nearly linear Mg-H-H , although the low $\text{MgH}(v=1)/\text{MgH}(v=0)$ ratio of 0.65 ± 0.10 for this component seemed inconsistent with an abstraction mechanism. Other suggested mechanisms for the low J component involved nearly linear release from an H-Mg-H geometry or secondary encounters of highly rotating MgH with H in the exit channel. The estimated population ratio $\text{MgH}(v=1)/\text{MgH}(v=0)$ was 0.7 ± 0.2 , with a large error estimate because of the extrapolated populations of the high J component in each vibrational level. This ratio was consistent with their statistical expectations. The p.e.s.'s for this reaction display interesting differences from the p.e.s.'s for the $\text{O}(^1\text{D}) + \text{H}_2$ reaction. In C_s symmetry, the ground state $\text{Mg}(^1\text{S}_0) + \text{H}_2$ and $\text{Mg}(^1\text{P}_1) + \text{H}_2$ surfaces are both of $^1\text{A}'$ symmetry and thus avoid each other. The lower $^1\text{A}'$ surface is repulsive, while the upper surface is attractive for insertion geometries. Only the lower $^1\text{A}'$ surface correlates with $\text{MgH}(\text{X}^2\Sigma^+)$ products. A surface crossing was therefore required during the course of the reaction. This crossing is possible in C_{2v} geometry, since the upper and lower $^1\text{A}'$ states become $^1\text{B}_2$ and $^1\text{A}_1$ states respectively (which do cross). This is an argument in favor of both components of the product rotational distribution having been products of some insertion mechanism: for the reaction to proceed at all, the required surface crossing would be much more probable for geometries close to the C_{2v} insertion pathway.

While the detailed suggestions for the microscopic dynamics of insertion reactions may be interesting to imagine, it is the author's feeling that such explanations outstrip the current knowledge of the potential energy surfaces involved. Perhaps a more appropriate way to view the expected vibrational distributions of $\text{O}(^1\text{D}) + \text{HX}$ reactions for $\text{X} = \text{H}, \text{Cl}, \text{Br}$ is to adopt a less detailed view. The product state distribution may be

considered to be related to which modes of the highly excited complex are excited during the insertion process. For $O(^1D) + H_2$ and $Mg(^1P_1) + H_2$ reactions, which involve a high degree of symmetry in the potential and the masses, high excitation of the bending mode is expected. The symmetric stretch should be of secondary importance and the asymmetric stretch is also expected to be of lesser import. Dissociation occurs when more than some critical amount of energy is present in an asymmetric stretch mode. In $O(^1D) + HX$ reactions as X is changed from H to Cl to Br, the degree of asymmetry is increased both by virtue of increasing disparity in the masses of the HX constituents and also by the differences in the respective potential energy surfaces. The bending mode will still be the most excited one in the complex, but the amount of energy channeled into the asymmetric stretch mode of the complex will increase. Just as rotation in the complex yields rotation of the products, vibration in the complex is expected to yield vibration in the products. A dissociation which occurs with more energy in the asymmetric stretch should result in higher product vibration and translation. Therefore one expects the amount of vibrational excitation in the products of reactions of $O(^1D)$ with H_2 , HCl and HBr to increase as the size and mass of the halide atom is increased.

CHAPTER 5

(5.1) Introduction: $O(^1D) + HBr$

The reaction of $O(^1D)$ with HBr ,

has received much less attention than homologous reactions of $O(^1D)$ with H_2 or HCl . It has been studied by Wine, Wells and Ravishankara¹⁰⁸ using resonance fluorescence techniques to monitor the $O(^3P)$ and $H(^2S)$ concentrations. They determined the total rate constant to be $k_5 = (1.48 \pm 0.16) \times 10^{-10} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$. This is equal to their rate constant for the $O(^1D) + HCl$ reaction, and slightly higher than the $O(^1D) + H_2$ rate constant of $(1.0 \pm 0.1) \times 10^{-10} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ determined by Force and Wiesenfeld¹³³. For comparison, the rate constant for the $O(^1D) + HF$ reaction was estimated by Wine et al.¹⁰⁸ to be $(1.5 \pm 0.9) \times 10^{-10} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$.

No theoretical studies or LIF experiments are known of concerning the $O(^1D) + HBr$ reaction, although the $O(^3P) + HBr$ reaction has been the subject of some recent investigation experimentally^{134,135,136,137} and theoretically^{138,139}. The reaction with $O(^3P)$ may be understood as a direct abstraction mechanism, with substantial inversion in the vibrational (about 95% into $OH(v=1)$ ^{135,139}) and rotational¹³⁹ distributions of the OH product resulting from the kinematic constraints of a $H + LH$ mass combination on a potential energy surface favoring a collinear reaction path. The effects of differing reagent masses on the appearance of a collinear trajectory may be simulated by skewing the collinear surface by an angle depending on the masses involved. The collinear

surface for a $\text{H} + \text{LH}$ mass combination is very highly skewed. The kinematic effects of highly skewed, collinear surfaces with reaction barriers on trajectories are exemplified by "corner-cutting" trajectories¹⁴⁰. Such trajectories also explain the large enhancements in reaction rate for vibrationally excited reagents. The reaction complex shows no evidence of crossings onto the singlet surface: product distributions are modelled well by trajectories solely on the triplet surface. This well-understood reaction mechanism is in contrast with $\text{O}(^1\text{D})$ reactions, which are typified by insertion mechanisms on potential energy surfaces with large intermediary potential minima, but which also have yielded inverted product energy distributions.

In the single known study of the $\text{O}(^1\text{D}) + \text{HBr}$ reaction, Wine et al. determined the branching ratios to be $(80 \pm 12)\%$, $<4.5\%$ and $(20 \pm 7)\%$ for reactions (5a-c) respectively. Among the series H_2 , HCl and HBr , the branching ratio for the quenching channel increased from $<4.9\%$ for H_2 to $(9 \pm 5)\%$ for HCl and to $(20 \pm 7)\%$ for HBr . Assuming a similar region of configuration space existed for $\text{O}(^1\text{D}) + \text{HBr}$ and $\text{O}(^1\text{D}) + \text{HCl}$ reactions in which the first excited singlet and triplet states were energetically close, the transfer from a singlet to a triplet potential energy surface in reaction (5c) would then have been even less forbidden than in the $\text{O}(^1\text{D}) + \text{HCl}$ reaction because of the breakdown of strict angular momentum coupling schemes as one progresses towards heavier atoms. One new feature in this reaction was the large (~ 46 kJ/mol) energy splitting of the $\text{Br}(^2\text{P})$ states with the sum of spin and electronic angular momentum either $1/2$ or $3/2$. The increased exothermicity of the $\text{O}(^1\text{D}) + \text{HBr}$ reaction allowed population of $\text{OH}(\nu \leq 5)$, instead of $\text{OH}(\nu \leq 4)$ as in the HCl and H_2 reactions.

Even though the channel producing BrO was slightly more exothermic than for the $\text{O}(^1\text{D}) + \text{HCl}$ case, the BrO product represented a minor product channel. Instead, Wine et al. found the OH product channel to be possibly more important for the $\text{O}(^1\text{D}) + \text{HBr}$ reaction $((80 \pm 12)\%)$ than for the $\text{O}(^1\text{D}) + \text{HCl}$ reaction $((67 \pm 10)\%)$. This may

have been due to some unknown difference in the potential energy surface. It is possible that the increased exothermicity of the OH + Br channel may have been important.

It was also found by Wine et al.¹⁰⁸ that the BrO product channel accounted for less than 4.5% of the products of the O(¹D) + HBr reaction, while the ClO channel represented (24 ± 5)% of the products of the O(¹D) + HCl reaction. The 11 kJ/mol ²Π_{1/2}-²Π_{3/2} splitting of BrO compared to the analogous 4 kJ/mol splitting of ClO is not expected to modify the product state densities of this channel enough to explain the more minor branching into the BrO channel.

(5.2) O(¹D) + HBr Experimental Details, Results and Discussion

All results for the O(¹D) + HBr reaction were obtained using the 11/83 data acquisition system. The pressures of ozone and HBr were (10 ± 1.5) mTorr each. The total pressure was maintained at (20 ± 1) mTorr. The spectra were recorded at 40 μs increments, beginning 20 μs before the ozone photodissociation laser pulse and continuing until 540 μs after the initiation of the reaction. The analyzed set of spectra was the result of 844 set of complete interferograms.

It was only possible to obtain two days worth of data for this reaction because of a laboratory mishap. The resulting spectra were of poorer SNR than those obtained for the HCl reaction. Nevertheless, both OH and HBr peaks were clearly evident in the spectra, samples of which are displayed in figure 32. The OH peaks relaxed and became indistinguishable from the noise much more quickly than for the HCl reaction (see figure 28). This could indicate that HBr had a larger cross section than HCl for the vibrational relaxation of OH, although this may have been only an effect of the lower SNR in these

Figure 32: Samples of time delayed spectra for the O(¹D) + HBr reaction. The spectra are noisy, and OH emissions fade quickly. Emissions from HBr increase with time.

spectra. The secondary V-V energy transfer from excited OH products to leftover HBr($v=0$) was also noticeable in the spectra, although the HBr signals were not clear enough to allow any worthwhile quantitative analysis: the prompt HBr production was barely perceptible in the raw spectrum.

The OH product was only analyzable for the first 300 μ s and the results of this analysis are shown in table XI. The vibrational distributions are plotted in figure 33. Unrealistic variations were seen in the OH($v=1$) population because of the high uncertainties involved in the analysis of the noisy spectra. The initial vibrational distribution of OH peaked in $v=4$ and 5. The normalized initial distribution of excited OH was found to be $P_{OH}(v=1:2:3:4:5) = (8\pm3): (11\pm3): (18\pm2): (31\pm4): (32\pm5)$. This distribution is shown on an energy level diagram and compared to the $O(^1D) + HCl$ distribution in figure 34. The GI distribution from the $O(^1D) + HBr$ reaction was more inverted vibrationally than the OH distribution from the $O(^1D) + HCl$ reaction ($P_{OH}(v=1:2:3:4) = (4\pm2): (19\pm2): (42\pm3): (34\pm3)$); however, both distributions channeled about the same fraction of their exothermicity into product vibration. The fractions of the exothermicity which ended up as product vibration (based *solely* on the excited vibrational distribution) were $f_{v^*} = (57\pm7)\%$ for the HBr reaction and $f_{v^*} = (67\pm5)\%$ for the HCl reaction. Both reactions channeled about 60% of their exothermicity into vibrational energy of the product. This is to be compared with $f_{v^*} = 43\%$ obtained by previous chemiluminescence measurements of the $O(^1D) + H_2$ reaction⁷³. These measurements, when combined with LIF results for the OH($v=1$)/OH($v=0$) ratio measured at similar reactant collision energy, yielded an estimated initial distribution of $P_{OH}(v=0:1:2:3:4) = 22: 23: 25: 20: 10$. This OH vibrational distribution for the $O(^1D) + H_2$ reaction was less inverted than the distribution obtained for the $O(^1D) + HCl$ and $O(^1D) + HBr$ reactions.

**Table XI: Populations of Rovibrational Levels;
OH Product of the O(¹D) + HBr Reaction**

Time Delay (μ s)		Populations of J-levels of OH($X^2\Pi_{3/2}$) (arbitrary units) derived from P-branch lines						
		J=1	J=2	J=3	J=4	J=5	J=6	Total
20	v=1	13	9	12				35 $\pm$ 14
	v=2	13	17	10	5	4	3	53 $\pm$ 12
	v=3	27	24	14	9	10		85 $\pm$ 10
	v=4	37	49	32	16	10		144 $\pm$ 19
	v=5	41	54	34	20			149 $\pm$ 25
							$\Sigma =$	465 $\pm$ 38
60	v=1	19	11	12				42 $\pm$ 17
	v=2	26	31	14	10	5	9	96 $\pm$ 15
	v=3	43	39	28	15	8		133 $\pm$ 14
	v=4	57	55	33	20	7		172 $\pm$ 19
	v=5	14	36	21	11			82 $\pm$ 20
							$\Sigma =$	525 $\pm$ 38
100	v=1	10	12	11				32 $\pm$ 16
	v=2	27	29	17	10	6	7	96 $\pm$ 13
	v=3	46	38	27	12	7		131 $\pm$ 13
	v=4	38	47	25	15	4		129 $\pm$ 17
	v=5	27	21	8	7			62 $\pm$ 19
							$\Sigma =$	449 $\pm$ 36
140	v=1	27	19	11				57 $\pm$ 15
	v=2	27	25	11	8	5	6	82 $\pm$ 13
	v=3	34	32	19	8	4		97 $\pm$ 14
	v=4	26	28	17	8			79 $\pm$ 12
							$\Sigma =$	315 $\pm$ 27
180	v=1	19	11					30 $\pm$ 12
	v=2	21	23	11	8	5		67 $\pm$ 12
	v=3	25	24	18	9	3		79 $\pm$ 11
	v=4	21	18	9	8			57 $\pm$ 11
							$\Sigma =$	232 $\pm$ 23
220	v=1	13	9					21 $\pm$ 14
	v=2	14	18	11	5	4		51 $\pm$ 10
	v=3	20	18	10	6			53 $\pm$ 9
	v=4	16	18	8	4			46 $\pm$ 11
							$\Sigma =$	172 $\pm$ 22
260	v=1	17	9	7				34 $\pm$ 14
	v=2	16	12	7	6			40 $\pm$ 9
	v=3	12	13	7	5			37 $\pm$ 8
	v=4	0	7	5				12 $\pm$ 5
							$\Sigma =$	123 $\pm$ 19
300	v=1	14	11	8				34 $\pm$ 16
	v=2	0	10	6	3			19 $\pm$ 7
	v=3	0	6	6	3			15 $\pm$ 5
							$\Sigma =$	68 $\pm$ 19

Figure 33: Time dependent vibrational distribution of OH produced in the $\text{O}(^1\text{D}) + \text{HBr}$ reaction. The time delay increases towards the front of this figure.

Figure 34: Correlation diagram and initial OH vibrational distribution for the $O(^1D) + HBr$ reaction, as in figure 30. This figure also displays the OH distribution from the $O(^1D) + HCl$ reaction at the extreme right hand side of the figure. The ground state HOBr energy was taken from reference 48. In this figure, excited state HOBr energies were assumed to be similar to those of HOCl.

Although the further analysis of these results requires more detailed experimental study, the results thus far displayed may be qualitatively explained by a dynamical model similar to that presented for the $O(^1D) + HCl$ reaction: a large asymmetry in the mass combination and the p.e.s. causes the dominant insertion approach of $O(^1D)$ to HBr to excite the asymmetric stretch of the $HOBr$ complex to a higher degree than for the $O(^1D) + H_2$ reaction. This $H + LH$ p.e.s. thus leads to higher vibrational excitation of the diatomic product.

The reduced depth of the $HOBr$ well compared to the HOH well, as well as the higher mass of the Br atom, reduces the forces favoring a more perpendicular $O(^1D)$ approach to the HR reactant. Therefore the distribution of "angles of approach" (as defined by Fitzcharles and Schatz¹²⁰) should display larger variation from the energetically optimum insertion angle and this may also contribute to increased excitation of the asymmetric stretch mode of the complex. In this manner the reduced well depth of the $HOBr$ and $HOCl$ potential energy surface proffers a second mechanism whereby increased product vibration may be observed.

The branching ratio of 20% for the primary quenching reaction indicated that the first excited singlet and triplet states may again have been close in energy over a substantial range of geometries and that a significant portion of encounters may have occurred along these surfaces. Thus any reactions which might have occurred on the excited singlet surface and did not cross to the triplet manifold would again have been subject to a repulsive exit-channel $Br-OH$ force resulting from the (energetically preferred) collinear reaction dynamics of the $^1\Pi$ state. Such an abstraction channel would promote vibrational excitation of the OH product. Since the preferred excited state geometry in the exit channel is collinear, this repulsive energy release would not tend to excite rotational modes of the OH product. A repulsive energy release late in the exit channel may result in substantial product translation for reactions occurring upon

collinear surfaces which are only slightly skewed (e.g. L + HH mass combinations). Recall that the skewing angle is the angle between the R_{AB} and R_{BC} axes in a coordinate system in which the trajectory may be simulated by letting a ball of unit mass roll along the surface. However, the skewing angles for the $O(^1D) + HCl$ and $O(^1D) + HBr$ reactions were $\beta = 16.9^\circ$ and $\beta = 15.4^\circ$ respectively, as calculated by the formula¹⁴¹

$$\cos^2\beta = m_A m_C / ((m_A + m_B)(m_B + m_C)).$$

This means that "corner-cutting" trajectories, in which trajectories could enter the exit channel without ever sampling regions of small R_{AB} or R_{BC} were possible. On such highly skewed surfaces product energy will be channeled into vibrational modes of the departing diatomic more efficiently than on only slightly skewed surfaces. Thus the possibility that a fraction the reactive encounters occur on the highly skewed $^1\Pi$ excited state surface is a third mechanism which favors the formation of high vibrational levels of the product OH.

It is unfortunate that details of the electronic surfaces involved in the $O(^1D) + HBr$ reaction are presently unknown. For example, if the excited state $^1A''$ and $^3A'$ crossing were unavailable to reaction, doubt would also be cast on the quenching mechanism proposed in the previous chapter for the $O(^1D) + HCl$ quenching reaction involving the analogous excited states. More detailed knowledge of the singlet surfaces is also required to explain the anomalously low branching into the BrO channel as compared to the ClO channel. The vibrational distributions of the excited OH product were very much like those obtained for $O(^1D) + HCl$. The overall dynamics for both HBr and HCl reactions are suggested to be a consequence of: (1) the mass combination and the reduced well depth on an asymmetric p.e.s., with insertion geometries leading to asymmetric stretching of the HOX intermediate followed by vibrational and rotational excitation in the product OH and (2) the possibility of collinear abstraction reactions on the excited $^1\Pi$ collinear surface yielding primarily vibrational excitation in the product OH.

(5.3) Introduction: $O(^1D) + H_2S$

Two investigations of the reaction of $O(^1D)$ with H_2S ,

have been undertaken in the past decade. Detailed information about rate constants and branching ratios is unavailable for this $O(^1D)$ reaction. Studies of the $O(^1D) + H_2S$ reaction have investigated the internal state distribution of the OH product. In the analogous $O(^3P)$ reaction with H_2S ^{142,143} both SH and HSO product channels were shown to be possible, with more than 50% of the total products of the triplet reaction forming OH + SH and less than 20% forming HSO + H. The latter products are definitely present, as shown in a reactive scattering experiment which detected a backward-scattered HSO product¹⁴⁴.

For $O(^1D)$ however, the homologous reaction with H_2O has received much attention^{50,57,59,60,145,146}, being of greater importance in stratospheric chemistry. The rate of the H_2O reaction^{145,147,148} is $\sim 2.0 \times 10^{-10} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$. This rate has been shown to be relatively independent of the translational energy of the $O(^1D)$ in the absorption experiments of Gericke and Comes^{60,145} detecting the OH product. Two initial studies reported bimodal rotational distributions in the $OH(v=0)$ product^{50,149}. Later studies of the reaction of $^{16}O(^1D)$ with isotopically labelled $H_2^{18}O$ allowed the separation of ^{16}OH and ^{18}OH spectra. The ^{18}OH product was a remnant of the original $H_2^{18}O$ reagent while the ^{16}OH product was newly formed in the reactive encounter. The rotational distributions of both the ^{18}OH and the newly formed ^{16}OH products were the same in the ground vibrational state, but the higher vibrational levels were populated

almost exclusively by the newly formed ^{16}OH bond^{57,59,146}. The probability of simultaneous production of two vibrationally excited OH molecules was negligible⁵⁹. Gericke and Comes monitored the formation of the OH product instead of the rate of $\text{O}(^1\text{D})$ consumption as in resonance fluorescence experiments. Since the experiments of Gericke and Comes^{58-60,145,146} used a UV laser absorption technique they were not subject to problems involving predissociation of the excited $\text{OH}(^2\Sigma^+)$ electronic state (only a restricted range of vibrotational levels are measurable in LIF experiments probing the $\text{OH}(X^2\Pi)$ distribution). The absorption technique allowed the probing of higher rovibrational levels than in LIF experiments and the vibrational product distribution of the newly formed OH was determined to be $P_{\text{OH}}(v=0:1:2) = 69:22:9$. Gericke and Comes found the fraction of energy released as rotation, 20%, was smaller than expected. Sixty percent of the product energy was estimated to have been released as translational energy. Gericke and Comes also determined that H_2O was very efficient at thermalizing the translational and rotational energy of excited OH: they determined the thermalization to occur at a gas kinetic rate and explained this as a result of the ability of OH and H_2O to form long-range hydrogen bonds.

Up to 14% of $\text{O}(^1\text{D}) + \text{H}_2\text{O}$ reactive encounters result in quenching of the oxygen atom¹⁴⁷, and less than 1% form¹⁵⁰ the $\text{H}_2 + \text{O}_2$ reaction products. Thus ~86% of the products are formed in the OH + OH channel. Such a rate constant and branching ratio is akin to the results presented for the $\text{O}(^1\text{D}) + \text{HCl}/\text{HBr}$ reactions, and one expects the $\text{O}(^1\text{D}) + \text{H}_2\text{S}$ reaction to conform: the $\text{O}(^1\text{D}) + \text{H}_2\text{S}$ reaction probably channels more than 80% of its products into OH and SH and the rest of its encounters result in quenching of the $\text{O}(^1\text{D})$ and vibrational/rotational excitation of the reagent, H_2S . Note, however, that the channel producing $\text{HO}_2 + \text{H}$ has been ignored since it is endothermic. This may not be a good approximation for the $\text{O}(^1\text{D}) + \text{H}_2\text{S}$ reaction. A large branching ratio of 50% was suggested by Klee, Gericke and Comes⁸³ (by comparison with the

O(³P) reaction) for the HSO + H channel of the homologous O(¹D) + H₂S reaction is valid.

As with H₂O, relaxation of the rotational and vibrational energy of the product OH is expected to be fast. Since HCl and HBr also are able to form hydrogen bonds with OH, the rate of vibrational relaxation of the OH product in HCl, HBr and H₂S (H₂O) systems is expected to be roughly similar and is limited by the collision frequency.

After the laser absorption experiments with the O(¹D) + H₂O reaction, Klee, Gericke and Comes⁸³ used LIF to probe the internal state distribution of the OH product of the O(¹D) + H₂S reaction. They determined the rotational distributions of the OH(v=1) and OH(v=0) products to be highly inverted and describable by Boltzmann distributions with $T_{v=0} = 2300 \pm 100$ K and $T_{v=1} = 2650 \pm 150$ K. The population ratio $P_{OH(v=1)}/P_{OH(v=0)} = 0.17$ was observed. By calibration with their absolute absorbance measurements for the O(¹D) + H₂O reaction, they determined that 25% of all reactive encounters led to formation of OH in the ground and first excited vibrational levels.

An early FTIR emission experiment⁸⁰ has also investigated the initial vibrational distribution of the OH product of the H₂S reaction. In these experiments the excimer laser was not synchronized to the interferometer sweep, so no time resolved results were possible. At the flow rates and pressures used, the products suffered about 100 collisions in the observation zone: changes were observed in the measured vibrational distribution when different reagent mixtures were used. Thus the observed vibrational distribution of $P_{OH(v=1:2:3:4:5)} = 15: 27: 30: 22: 6$ formed a lower limit for the amount of initial vibrational excitation in the OH product of reaction (6). This lower limit was itself much more inverted than the vibrational distributions measured for the O(¹D) + H₂O reaction (see above). It was pointed out⁸⁰ that since this study used no buffer gas, while Klee, Gericke and Comes used He as a buffer gas and used a lower energy photolysis laser to

produce their $O(^1D)$, the initial translational energy of the $O(^1D)$ was higher in these FTIR experiments. It was suggested that part of the increased vibrational inversion could be due to the increased kinetic energy of the $O(^1D)$, even though the effect of translational energy on the rate of the analogous $O(^1D) + H_2O$ reaction had been shown to be minimal¹⁴⁵.

The combination of the UV absorption and IR chemiluminescence results led to an estimate of the initial vibrational distribution of OH which was bimodal: $P_{OH}(v=0:1:2:3:4:5) = 47: 8: 14: 16: 12: 3$. Since the IR chemiluminescence measurements were not time resolved while the LIF experiment was, the indication of an inverted vibrational distribution for $OH(v>0)$ is particularly important to confirm under more carefully controlled conditions in which the number of collisions (and thus the probability of secondary reaction and the extent of relaxation) is small. In particular, it must be ascertained that the bimodal distribution is not simply a result of a secondary reaction.

In the combined estimate of the total vibrational distribution, 25% of the energy available to the products of reaction (6a) was represented as vibrational energy of OH. This was similar to the 20% fraction of available energy present as vibration in the newly formed OH bond for the $O(^1D) + H_2O$ reaction⁵⁹. When combined with the absolute calibration of Klee, Gericke and Comes⁸³, this implied that ~50% of the reaction did not form OH. Klee, Gericke and Comes suggested that channel (6d), forming $HSO + H$, was a likely candidate by comparison with the branching ratio for the $O(^3P)$ reaction; however, the extent of the quenching channel (6c) is also unknown for reaction (6). Although reaction (6b), forming $H_2 + SO$, is highly exothermic it is expected to be of lesser importance because this channel involves substantial rearrangement of the expected $HSOH$ complex before the H atoms get close and because the analogous $H_2 + O_2$ channel of the $O(^1D) + H_2O$ reaction has been shown to be unimportant.

(5.4) $\text{O}(^1\text{D}) + \text{H}_2\text{S}$ Experimental Details, Results and Discussion

The same reagent pressures, flow rates and time delays were used in studies of reaction (6) as in the measurements of the $\text{O}(^1\text{D}) + \text{HBr}$ reaction. To obtain the spectra used in the population analysis, 572 complete interferograms were coadded.

Table XII presents the results of the population analysis. The time dependence of the observed vibrational populations is displayed in figure 35. Considerable uncertainty was present in these determinations. The vibrational distribution at the earliest time delay of 20 μs was $P_{\text{OH}}(v=1:2:3:4:5) = (11 \pm 7): (13 \pm 5): (17 \pm 4): (30 \pm 5): (28 \pm 10)$, corresponding to an estimate of $f_{v'} = (60 \pm 9)\%$ for the maximum fraction of exothermicity converted into product vibration. The decay and vibrational relaxation of the OH product was similar to that obtained in the $\text{O}(^1\text{D}) + \text{HCl}/\text{HBr}$ reactions, apart from the population of an extra vibrational level. The population of $\text{OH}(v=5)$ was undetectable by 180 μs after the reaction was initiated. The extremely fast decay of the highest populated vibrational state explained why it was mainly in the population of this state that these results differ from the earlier FTIR determinations which were not time resolved. As might be expected, each individual time delayed vibrational distribution of this experiment had a more strongly peaked shape than the time-averaged distribution reported in the earlier FTIR experiments.

The normalized vibrational distribution at the second time delay was $P_{\text{OH}}(v=1:2:3:4:5) = (8 \pm 4): (18 \pm 4): (22 \pm 3): (34 \pm 4): (18 \pm 6)$, which agreed with the earliest distribution within the estimated errors and yielded a maximum estimate of $f_{v'} = (57 \pm 6)\%$. However, the total observed population was maximized at the second time delay of 60 μs , at which time the total population was 30% higher than at the earliest time delay of 20 μs . For a primary reaction product one would expect the maximal

**Table XII: Populations of Rovibrational Levels;
OH Product of the $O(^1D) + H_2S$ Reaction**

Time Delay (μ s)		Populations of J-levels of OH($X^2\Pi_{3/2}$) (arbitrary units) derived from P-branch lines						
		J=1	J=2	J=3	J=4	J=5	J=6	Total
20	v=1	14	12	8				35 ± 20
	v=2	12	9	7	6	4		38 ± 15
	v=3	9	12	10	8	3	4	51 ± 13
	v=4	22	20	20	10	7	9	88 ± 16
	v=5	21	30	14	11	8		83 ± 31
							$\Sigma = 294 \pm 45$	
60	v=1	17	8	7				31 ± 16
	v=2	25	20	13	7	5		70 ± 14
	v=3	27	23	18	6	4	3	83 ± 12
	v=4	41	39	21	11	11	6	129 ± 14
	v=5	23	28	11	7			69 ± 21
							$\Sigma = 382 \pm 35$	
100	v=1	22	11	8				41 ± 14
	v=2	19	22	15	7	4		67 ± 13
	v=3	31	27	23	11	3	3	98 ± 12
	v=4	38	34	22	12	8	4	118 ± 13
	v=5	13	18	6				37 ± 18
							$\Sigma = 362 \pm 36$	
140	v=1	11	8	9				29 ± 14
	v=2	26	20	13	6	4		68 ± 12
	v=3	31	28	20	7	3	3	92 ± 11
	v=4	23	30	20	9	3	4	89 ± 12
	v=5	12	13					25 ± 16
							$\Sigma = 303 \pm 30$	
180	v=1	22	8	7				37 ± 13
	v=2	20	16	11	6			53 ± 11
	v=3	23	30	16	11	5	2	87 ± 12
	v=4	20	18	14	6			58 ± 10
							$\Sigma = 235 \pm 23$	
220	v=1	11	6	7				24 ± 12
	v=2	21	17	8	6			51 ± 10
	v=3	25	26	16	7	8	2	83 ± 9
	v=4	9	11	8	5			33 ± 9
							$\Sigma = 191 \pm 20$	

260	v=1	13	14				27 ± 11
	v=2	22	14	9	3		48 ± 9
	v=3	27	28	11	6	3	75 ± 9
	v=4	7	9	5			21 ± 9
							$\Sigma = 171 \pm 19$
300	v=1	19	5				24 ± 10
	v=2	11	12	7	5		34 ± 9
	v=3	17	17	11	4	4	53 ± 9
	v=4	8	7	5			21 ± 9
							$\Sigma = 132 \pm 18$
340	v=1	13	10				23 ± 10
	v=2	14	11	8	4		37 ± 9
	v=3	17	18	6	4		45 ± 9
	v=4	7	5	3			15 ± 9
							$\Sigma = 119 \pm 19$
380	v=1	0	12	7			18 ± 9
	v=2	12	12	8	4		35 ± 9
	v=3	19	12	6	3		40 ± 8
	v=4	8	6	4			17 ± 10
							$\Sigma = 111 \pm 18$
420	v=1	16	7	11			33 ± 14
	v=2	12	11	9	5		37 ± 9
	v=3	15	15	6	2		38 ± 9
	v=4	8	5				12 ± 8
							$\Sigma = 120 \pm 20$
460	v=1	0	11	7			18 ± 10
	v=2	17	5	7	4		34 ± 7
	v=3	7	12	6	3		27 ± 9
	v=4	8	5				12 ± 7
							$\Sigma = 92 \pm 17$
500	v=1	0	8	9			17 ± 8
	v=2	10	10	4			24 ± 8
	v=3	7	9	5	4		25 ± 8
	v=4	7	4	4			16 ± 9
							$\Sigma = 68 \pm 19$
540	v=1	0	12				12 ± 5
	v=2	11	5	6			22 ± 9
	v=3	9	8	7			23 ± 7
	v=4	6	5	5			16 ± 9
							$\Sigma = 72 \pm 15$

Figure 35: Time dependent vibrational distribution of OH produced in the $\text{O}(^1\text{D}) + \text{H}_2\text{S}$ reaction. The time delay increases towards the front of this figure.

population to occur at the first time delay, which corresponds roughly to two gas kinetic collisions, rather than at the second time delay at roughly six gas kinetic collisions. The percentage increase in population at the second time delay was smaller for the reactions of $O(^1D)$ with HCl and HBr (0% and 12% respectively). There are several possible reasons for the lack of population at the earliest time delay.

One explanation for such behavior assumes that the total population in high rotational states of lower vibrational levels was significant but that the population of each rovibrational level individually was too small to be noticed at the SNR ratio of the spectrum. Higher rotational states which would not have appeared for SNR reasons at the earliest time delay would have had ample time to relax by 60 μ s and increase the apparent population of the lower vibrational levels. However, this is not considered likely, since the OH product of the HCl and HBr reactions is known to be rotationally excited too, but the percentage increase in population is markedly different in a system where the rate constants for rotational relaxation of OH are expected to be of the same order of magnitude. Furthermore, this explanation would lead one to expect the bulk of the "missed" population to be in the lowest vibrational levels. This is inconsistent with the similarity of the normalized distributions at the first and second time delays.

Another explanation entails the entry of reaction products produced outside the observation zone into the observation zone. This would cause an increase in the observed population. The rates of HCl, HBr and H_2S reactions are all roughly gas kinetic and care was taken to reproduce the position of the reagent inlets and excimer pulse with respect to the mirror assembly defining the Welsh cell from experiment to experiment; however, the Welsh cell mirrors and excimer laser mirrors were adjusted for maximal intensity of the total IR signal prior to each experiment, so this explanation cannot be ruled out.

A third possibility involves secondary reactions populating excited levels of OH. This possibility was investigated using a computer model of the reacting system. The two possible secondary sources of OH were the reactions

To produce as much secondary reaction as possible, the rate constants for these two reactions were set at $\sim 1 \times 10^7 \text{ Torr}^{-1} \text{ s}^{-1}$ (roughly gas kinetic) and $\sim 1 \times 10^6 \text{ Torr}^{-1} \text{ s}^{-1}$ respectively. Both estimates of these rate constants were purposefully high since the object of the simulation was to see whether a 30% increase in the population of vibrationally excited OH was attainable. Furthermore, the population of the secondary OH product was assigned the same vibrational distribution as that of the primary distribution, even though the $\text{H} + \text{O}_3$ reaction is known¹⁵¹ to populate $\text{OH}(v>6)$ almost exclusively. The H atom reacting in (7b) was produced by channel (6d) of the primary reaction, which was assigned a branching probability of 50%, as suggested by the calibration of Comes combined with the earlier chemiluminescence data (as discussed in the previous section). The total population of $\text{OH}^\dagger$ peaked $\sim 32 \mu\text{s}$ after the reaction was initiated and was only 3% higher than the population at a $20 \mu\text{s}$ time delay. The time delay for which this maximum population represented a 30% increase was under $10 \mu\text{s}$. Clearly, a 30% increase in population from the $20 \mu\text{s}$ time delay to the $60 \mu\text{s}$ time delay cannot be explained by such a model. All attempts to simulate such behavior in a computer model using even more unrealistic variations of the estimated rate constants for reaction and relaxation processes failed to produce observed populations which required as long as $60 \mu\text{s}$ to peak and which also decreased thereafter to an appreciable extent. Thus the possibility of secondary reactions contributing to the apparent population increase is also considered very unlikely.

The possibility of all the OH products of reaction (6a) having populated only OH($v=0$) and OH($v=1$) was judged to be unlikely. Since the main purpose of this investigation was to measure the primary vibrational distribution of OH, and since the normalized vibrational distributions measured at both 20 and 60 μs time delays were the same within the error estimates, even though the total OH † population had apparently increased, the best estimate of the initial distribution was taken from the 60 μs time delay because the signal to noise ratio was significantly better at this time delay. This resulted in an estimated initial vibrational distribution for the OH product of the O(^1D) + H $_2$ S reaction of $P_{\text{OH}}(v=1:2:3:4:5) = (8\pm4): (18\pm4): (22\pm3): (34\pm4): (18\pm6)$.

The measurements of Klee, Gericke and Comes predicted $P_{\text{OH}}(v=1)/P_{\text{OH}}(v=0) = 0.17$, corresponding to $f_{v^*} < 3\%$ if the trend they observed continued. The combined estimate of the vibrational distribution obtained in this chapter with that of Klee, Gericke and Comes yielded an even more bimodal vibrational distribution of $P_{\text{OH}}(v=0-5) = 28: 6: 13: 16: 24: 13$ for $f_{v^*} = 40\%$, while the upper limit determined by the chemiluminescence measurements of this chapter was $f_{v^*} \leq (57\pm6)\%$. One might propose that the bimodal distribution be a result of two dynamically different reaction mechanisms. The studies of Cvetanovic et al. discussed previously in chapter 2 of O(^1D) + alkane reactions suggested that an abstraction mechanism whose products could not be quenched to form R $_{\text{OH}}$ by increasing the pressure was possible. Reactions of O(^1D) with the large and presumably sterically hindered alkanes cyclopentane and neopentane yielded 20% and 25% respectively of such an abstraction component, which was assumed to have reacted along O-H-R geometries. However such branching was observed to decrease in importance as the size of the alkyl R $\cdot$ group was decreased: Luntz's LIF experiments⁸² agreed with this observation and no "abstraction" component was noted for the O(^1D) + CH $_4$ reaction at all. It seems unlikely that the small H $_2$ S molecule would have ~60% branching into the "abstraction" channel populating the

higher vibrational levels as is suggested by the combined UV absorption and IRCL results. Such a dynamical branching has also been proposed¹⁵² for the $O(^1D) + H_2$ reaction in which the insertion component yielded products of low vibrational excitation while the vibrationally excited component corresponded to an abstraction mechanism; however, this quasiclassical trajectory study using a splined fit to the Schinke and Lester surface III¹¹⁸ found that while only 2% of the reactions could be classified as abstractions, the vibrational distribution was nevertheless inverted, peaking in $OH(v=3)$. Likewise, the previously discussed insertion mechanisms of Fitzcharles and Schatz¹²⁰ could also result in vibrational excitation and were not expected to produce mainly $OH(v=0)$. It would seem instead that the possibility of such a highly bimodal distribution in the $O(^1D) + H_2S$ reaction is itself suspect and bears further investigation, preferably in an experiment which is capable of measuring the population of *all* the vibrational levels simultaneously (an IR absorption experiment is one possibility). In accord with the previously suggested dynamics for $O(^1D) + HCl$ and $O(^1D) + HBr$, it is suggested that the vibrationally excited, inverted $OH^\dagger$ distribution is a result of insertion dynamics on an asymmetric potential with asymmetric masses.

(5.5) Introduction: $O(^1D) + CH_4$

Methane is one of the constituents of the stratosphere, and many studies have elucidated the rates and branching ratios for the reaction of $O(^1D)$ with methane¹⁵³. The recommended⁴⁷ overall rate for the reaction

is $k_g = 1.5 \times 10^{-10} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ over the temperature range 200-300 K. 90% of the reaction is ascribed to channel (a), producing OH and CH_3 , in the review of reference 48. It was also estimated that 10% of the reaction may populate channel (d), producing CH_2O and H_2 (although one molecular beam study ascribed this component to reaction producing $CH_3O + H$ instead⁷¹). The reaction rate is gas kinetic and the lowest potential energy surface involved has a very large well corresponding to the stable CH_3OH molecule. Formation of CH_3OH is exothermic by 564 kJ/mol (reaction (8e)).

Only a small number of studies have investigated the energy distributions of the primary reaction channel. A previous measurement from this laboratory⁷⁹ showed that the population of $OH(v=2)$ may be larger than that of $OH(v=1)$, and that $OH(v=3)$ and $OH(v=4)$ were also present. These experiments were not time-resolved, and emission from vibrationally excited CO, a product of a secondary reaction, was observed. Time-resolved spectra were later reported⁷³ in a doctoral thesis. At the earliest time delay, corresponding to 16 gas kinetic collisions, a lower limit to the initial vibrational distribution was measured to be $P_{OH}(v=1:2:3:4) = 38:31:23:8$. The measurements

made with the modified time resolved apparatus and presented in this chapter afford a better estimate of this initial vibrational distribution.

Luntz⁸² used LIF to probe the $\text{OH}(X^2\Pi)$ rovibrational distribution and found the populations of $\text{OH}(v=1)$ and $\text{OH}(v=0)$ to be approximately equal. The rotational distributions were broad and inverted. As in the $\text{O}(^1\text{D}) + \text{H}_2$ reaction, the mechanism was deduced to be an insertion into a C-H bond, forming a highly vibrationally excited alcohol, which very promptly decayed to yield the observed, nonstatistical vibrational and rotational distributions of the products.

Luntz also observed an "abstractive" component which formed 5% of the OH in rotationally cold states. This abstractive component became more important for larger hydrocarbons, reaching 90% for the reaction with $\text{C}(\text{CH}_3)_4$, and was tentatively assigned to be a result of the entrance channel crossing of the lowest singlet and triplet surfaces. This hypothesis was suggested by the similarity of the cold rotational component to that produced by reactions with $\text{O}(^3\text{P})$. In comparison with the $\text{O}(^1\text{D}) + \text{H}_2$ reaction, for which the "lifetime" of the HOH complex was quoted⁸² as approximately 0.35 ps, the lifetime of the CH_3OH collision complex was around 0.8 ps. The short lifetime of the CH_3OH complex had previously been established in quenching studies, which found that the methanol intermediate could be stabilized only at high pressures¹⁵⁴ or if the reaction was run in liquid Ar¹⁵⁵. Lifetimes for larger hydrocarbons increased dramatically (≥ 4 ps for $\text{O}(^1\text{D}) + \text{C}_2\text{H}_6$, etc.); however, the motions undertaken by the collision partners for the $\text{O}(^1\text{D}) + \text{CH}_4$ reaction are still likely to be analogous to those undergone in $\text{O}(^1\text{D}) + \text{HR}$ reactions for $\text{HR} = \text{H}_2, \text{HCl}$ and HBr .

Luntz also found that the Λ doublet selectivity decreased, and that less energy was channeled into the OH product for reactive partners larger than CH_4 . This indicated that internal modes of the OH's partner were becoming increasingly important. However, the vibrational and rotational surprisals¹⁵⁶ (a measure of the deviation of the

distribution from that expected statistically) continued to increase with the size of the partner.

Early investigations of the $O(^1D) + CH_4$ reaction include the flash photolysis experiments of Basco and Norrish⁷⁰, in which vibrationally excited OH was detected and a weak absorption tentatively assigned to CH_2O was detected.

Reaction (8) was studied in liquid Ar a few years later by DeMore and Raper¹⁵⁵, who found collisionally stabilized CH_3OH to be the major product. Reactions occurring in liquid Ar were assumed to proceed with almost no activation energy. Another reaction which was noted in this system was that of CH_3 with O_3 , and by addition of O_2 as a scavenger of CH_3 radicals it was shown that each CH_3 radical results in the destruction of at least two O_3 molecules. This study also demonstrated that the reaction of OH with O_3 had a nonzero activation energy.

Several years later, Li and DeMore¹⁵⁴ studied the $O(^1D) + CH_4$ reaction in the gas phase at high pressures. $O(^1D)$ was formed by irradiation of N_2O/RH mixtures at 185 nm. Typical partial pressures were 10 Torr of N_2O and 1 atm of CH_4 . At low pressures the OH product channel (reaction (8a)) was the main pathway. Reaction channel (8d) forming H_2 was measured to have a branching ratio of 9%. Since the previous study carried out in liquid Ar also had this branching ratio, it was concluded that the reaction mechanism for reaction (8d) did not involve the $[ROH]^*$ complex. This suggestion of alternate reaction mechanisms is reminiscent of the studies of Cvetanovic et al.⁷⁴⁻⁷⁷ discussed in chapter 2, which also showed that a component of $O(^1D) + RH$ reactions forming $R \cdot + OH$ also proceeded without passing through an $[ROH]^*$ geometry.

(5.6) $O(^1D) + CH_4$

Experimental Details, Results and Discussion

The reaction was run at the standard partial pressures for ozone and methane, and the normal set of time delayed interferograms was recorded with the 11/83 time resolved program. The final set of spectra analyzed was the result of 590 complete interferograms measured over two days of experiments.

The results of the population analysis are shown in table XIII. The time dependent vibrational populations are plotted in figure 36. Analysis of the earliest emission spectrum (20 μ s) yielded a normalized OH distribution of $P_{OH}(v=1:2:3:4) = (19\pm7): (32\pm5): (35\pm5): (14\pm5)$. This distribution was within the error estimates of the distribution at the second time delay (60 μ s): $P_{OH}(v=1:2:3:4) = (22\pm5): (38\pm4): (30\pm3): (10\pm3)$. As in the H_2S experiments, the total population of vibrationally excited OH apparently increased between the first and second time delays: the maximum population of excited OH was achieved at the third time delay (~ 10 gas kinetic collisions). This is thought to be an artifact, and could result from a combination of higher noise levels (resulting from radio frequency noise produced by the excimer discharge) and a broader rotational distribution causing population in less populated rovibrational states to be missed. This explanation would seem to be in disagreement with the small change in the normalized distribution when one considers that the population increases by a large amount ($\sim 60\%$ in the $O(^1D) + CH_4$ experiment) between the first and second time delays. Alternatively, the apparent population increase could be sensitive to the precise position of the Welsh cell mirrors. The final optimization of the collection optics was undertaken to achieve maximum IR signal height on each day of experimenting. Thus if the volume from which emissions were most efficiently collected and focussed onto the detector were physically lower in the reaction vessel, then the total population would

**Table XIII: Populations of Rovibrational Levels;
OH Product of the O(¹D) + CH₄ Reaction**

Time Delay (μ s)		Populations of J-levels of OH($X^2\Pi_{3/2}$) (arbitrary units) derived from P-branch lines							Total
		J=1	J=2	J=3	J=4	J=5	J=6	J=7	
20	v=1	27	10	8	10	8			63 ± 24
	v=2	32	25	18	15	8	5	5	108 ± 17
	v=3	27	24	28	17	7	7	6	117 ± 13
	v=4	13	12	9	14				49 ± 20
									$\Sigma = 337 \pm 40$
60	v=1	52	35	15	8				111 ± 33
	v=2	62	54	33	21	7	11		187 ± 19
	v=3	48	41	35	15	7	5		151 ± 17
	v=4	15	18	9	7				49 ± 15
									$\Sigma = 497 \pm 37$
100	v=1	66	42	22	8				137 ± 21
	v=2	63	53	33	19	6	10		185 ± 18
	v=3	46	40	31	15	4	4		140 ± 17
	v=4	20	15	6	7				47 ± 14
									$\Sigma = 510 \pm 36$
140	v=1	61	40	24	7				132 ± 21
	v=2	62	54	31	19	5	10		181 ± 17
	v=3	38	42	30	13	7	4		132 ± 15
	v=4	15	15	10	6				47 ± 12
									$\Sigma = 493 \pm 33$
180	v=1	65	42	25	9				140 ± 22
	v=2	60	53	33	17	6	7		175 ± 17
	v=3	41	36	25	11	5			117 ± 14
	v=4	18	13	8	6				45 ± 12
									$\Sigma = 477 \pm 34$
220	v=1	65	43	21	7				135 ± 20
	v=2	60	52	31	17	8	8		177 ± 17
	v=3	36	34	24	11	4			108 ± 12
	v=4	13	17	7	6				42 ± 11
									$\Sigma = 462 \pm 31$
260	v=1	59	43	20	6				128 ± 19
	v=2	57	52	31	16	5	6		166 ± 15
	v=3	33	31	21	10	4			98 ± 12
	v=4	12	11	5	4				32 ± 10
									$\Sigma = 424 \pm 29$

Figure 36: Time dependent vibrational distribution of OH produced in the $\text{O}(^1\text{D}) + \text{CH}_4$ reaction. The time delay increases towards the right in this figure.

apparently increase as a result of an initial influx of products into the observation zone. Such behavior would not affect the normalized distributions and is sufficient to explain the behavior exhibited by the OH product of the $O(^1D) + H_2S$ and $O(^1D) + CH_4$ reactions. However, in light of the size of the population increase and DeMore and Raper's observation that each CH_3 produced by reaction (8a) ultimately resulted in the destruction of two O_3 molecules, the possibility of secondary reactions affecting the present results could not be ruled out. The products of the $CH_3 + O_3$ reaction are unknown

In comparison to the previous chemiluminescence results, the present initial distribution was more inverted, the population of $OH(v=2)$ being almost double that of $OH(v=1)$. The expected slow vibrational relaxation was evident in the time dependence of the populations and was qualitatively similar to that exhibited by the OH product of previously discussed reactions of $O(^1D)$; however, the extent to which the total population of vibrationally excited OH decayed by the last time delay measured was significantly lower than in these other cases. The final population was ~60% of the maximally attained population for the $O(^1D) + CH_4$ reaction, while the final population for the $O(^1D) + H_2S$ reaction was less than 20% of the maximally attained population. If one assumes a negligible extent for secondary reactions producing $OH^\dagger$, the minimal decay in population must have been an effect of the change in reagent species to CH_4 from H_2S . It must then be concluded that methane was a much less efficient partner than H_2S (and HCl and HBr) for vibrational relaxation of OH. This is consistent with the expectation that vibrational relaxation take place more readily with partners which have dipole moments.

The maximum fraction of the reaction exothermicity channeled into product vibration was calculated to be $f_{v^*} = (55 \pm 4)\%$ using the distribution obtained at the first time delay. As in previous reactions presented in this thesis involving insertion reactions

on surfaces with intermediate wells, roughly 60% of the reaction exothermicity is channeled into product vibration using the populations measured in this thesis and assigning no reaction products to $\text{OH}(v=0)$. No difference was observed in the vibrational distribution of the product OH as a result of the internal structure of the methyl $\text{R}\cdot$ group. Thus it is suggested that the mechanism for the $\text{O}(^1\text{D}) + \text{CH}_4$ reaction was dynamically similar to that of the reactions for $\text{O}(^1\text{D})$ with hydrogen halides. The increased vibrational excitation of the OH product as compared to the product of the $\text{O}(^1\text{D}) + \text{H}_2$ reaction is suggested to have been the final result of the asymmetry in the potential surface and the asymmetry in the masses during the insertion geometries favored along the entrance channel.

Reactions of $\text{O}(^1\text{D})$ with related chlorofluorocarbon partners form the subject of a colleague's thesis⁶⁶ and alternate reaction dynamics involving the R group must be invoked to explain the primary production of HF (and HCl) in such reactions. Typically this primary hydrogen halide product was extremely excited rotationally and vibrationally. In such chlorofluorocarbon reactions the internal structure of the $\text{R}\cdot$ group obviously could not be ignored. Information regarding the comparable rearrangement to produce $\text{CH}_2\text{O} + \text{H}_2$ in the $\text{O}(^1\text{D}) + \text{CH}_4$ reaction could not be obtained from the present IR chemiluminescence experiments. For the purposes of explaining reaction (8a) only, it seems that the CH_3 group may be treated as a structureless mass, much as in reactions of $\text{O}(^1\text{D})$ with H_2 , HCl or HBr.

CHAPTER 6

(6.1) Summary and Conclusions

The first section of this thesis dealt with the use of bond functions to aid in the calculation of potential energy surfaces. Bond functions have been used to calculate potential energies for both diatomics^{10,11} and triatomics¹⁶⁻¹⁸. Their principal advantage is that these basis sets are typically much smaller than nuclear-centered basis sets of comparable quality, and therefore allow calculations to be performed on more complicated electronic systems. The approach is somewhat empirical in nature, and originated by optimizing the bond function basis set size with respect to the nuclear basis set size to reproduce a single, previously known feature of the potential surface. The potential usefulness of this method lies in the possibility that a simple procedure may exist by which one may predict which choice of bond function basis set will be optimum for calculations on systems for which no previously known features are available. Rather than continue previous calculation of the $O(^1D) + H_2$ potential energy surface¹⁷, it was decided to investigate the accuracy of the extension of bond functions basis sets from the diatomic regime, where they are known to produce excellent results, to triatomic calculations.

The merits of this bond function approach were investigated for H_2 and H_3 potential energy surfaces. Both H_2 and H_3 surfaces are well characterized. Nuclear basis sets, scaling factors for molecular environments and polarization function exponents were taken from literature results.

It was found that the accuracy of the triatomic calculation scaled qualitatively with the accuracy of the diatomic calculation, with two excellent choices of basis set for

H₂ being BF1 (a scaled DZP nuclear basis augmented by one set of optimized *sp* bond functions) and BF2 (a scaled TZPP basis with two sets of optimized *sp* bond functions). Both BF1 and BF2 bases were found to provide reasonable descriptions of the global energetics of the H₃ surface; however, BF2 resulted in a significantly decreased magnitude for the extent of local variations from parallelism to the "true" SLTH surface. The nature of these local variations on the H₃ surface was found to be related to the incompleteness of the H₂ limit. The diatomic incompleteness curve had a minimum incompleteness at the equilibrium H-H distance. This incompleteness and its local behavior were found to continue on the H₃ surface, roughly along the minimum energy path. BF1 and BF2 basis sets have more recently been applied to second row diatomics, for which excellent results were also obtained¹¹.

The implication of these results is that the use of the BF1 or BF2 bond function basis sets, while empirical in origin, should allow reasonable surfaces to be economically calculated in the future for O(¹D) + HX reactions (X = H, F, Cl). In particular, the analytical surface¹¹⁵ for the O(¹D) + HCl reaction is known to have had several flaws and it is felt that a calculation of the complete surface using a bond function basis could offer a substantially improved description.

The experimental observations of the IR emissions of the products of the O(¹D) + HCl reaction indicate that the product OH[†] was produced with substantial vibrational excitation. Initially produced HCl[†] was also observed. The capability of measuring the detailed time dependence of this emission indicated that vibrational energy transfer from OH[†] to unreacted HCl(*v*=0) reagent was occurring as a secondary process.

Based on previous work on the O(¹D) + H₂ and O(¹D) + HCl reactions, the dynamics of the O(¹D) + HCl reaction was explained as an insertion of O(¹D) into the HCl bond. Because of the asymmetric potential energy surface and the large difference in mass between H and Cl, this insertion would more strongly excite the asymmetric

stretch of the intermediate than for the $O(^1D) + H_2$ reaction. This increased stretching of the triatomic complex ultimately resulted in increased vibration of the OH product. In spite of the presence of the deep potential well on the HOCl potential energy surface, statistical vibrational energy disposal indicative of a long-lived intermediate was not seen. The presence of the primary HCl product, combined with a knowledge of the excited states of HOCl, led to the suggestion that dynamics occurring on the first excited singlet and triplet states of HOCl may also have been involved. The normalized initial distribution of the product of the $O(^1D) + HCl$ reaction was $P_{OH}(v=1-4) = (4 \pm 2): (19 \pm 2): (42 \pm 3): (34 \pm 3)$.

The crude data available for the $O(^1D) + HBr$ reaction suggested that the reactive dynamics was similar: HCl and HBr reactions with $O(^1D)$ deposited up to $(67 \pm 5)\%$ and $(57 \pm 7)\%$, respectively, of their available energy into vibration of the OH product. The initial OH distribution for the $O(^1D) + HBr$ reaction was $P_{OH}(v=1-5) = (8 \pm 3): (11 \pm 3): (18 \pm 2): (31 \pm 4): (32 \pm 5)$. The decay of the OH emissions was much faster for the HBr reaction than for the HCl reaction, indicating that HBr was a better quencher of $OH^\dagger$ than HCl is. The secondary V-V transfer from $OH^\dagger$ populating $HBr(v=1)$ was noted.

A reinvestigation of the $O(^1D) + H_2S$ reaction showed that previous indications of highly vibrationally excited OH, made in experiments which were not time-resolved, were indeed valid, in spite of indications⁸³ that production of $OH(v=0)$ was about six times more probable than production of $OH(v=1)$. The initial vibrational distribution was measured to be $P_{OH}(v=1-5) = (8 \pm 3): (11 \pm 3): (18 \pm 2): (31 \pm 4): (32 \pm 5)$, which represented $(57 \pm 6)\%$ of the exothermicity of the reaction. The quenching rate of $OH^\dagger$ by H_2S was found to be similar to that of HCl.

The $O(^1D) + CH_4$ reaction was also reinvestigated. The increased time resolution of the present IRCL technique resulted in a vibrational distribution for the product OH, $P_{OH}(v=1-4) = (22 \pm 5): (38 \pm 4): (30 \pm 3): (10 \pm 3)$, which was more inverted

than data obtained previously and represented $(55 \pm 4)\%$ of the reaction's exothermicity. The decay of emissions from OH^+ in this reaction was very slow. The possibility of secondary reactions also populating $\text{OH}(v>0)$ at longer time delays could not be ruled out for the $\text{O}(^1\text{D}) + \text{CH}_4$ reaction.

All four of these reactions of $\text{O}(^1\text{D})$ with simple hydrides, $\text{HR} = \text{HCl}, \text{HBr}, \text{H}_2\text{S}$ or CH_4 , indicated that up to $\sim 60\%$ of the exothermicity of the reactions was channeled into OH vibration. Thus it is likely that the dynamics in all four of these reactive systems may be explained by an insertion event on an asymmetric potential energy surface involving widely disparate masses for H and R.

The simplicity of the IR chemiluminescence technique indicates that the results of previous LIF experiments must be viewed with caution. The principal possibility for error in the chemiluminescence measurements is that rotational relaxation might not have occurred for the high rotational levels populated in the lower vibrational levels. This was not thought to have occurred significantly since the measured vibrational distributions did not change markedly during the early time delays. Nevertheless, measurements of $\text{OH}(v=0)$ are not possible with this chemiluminescence technique and there remains the possibility that some excited rotational states remained undetected in these measurements. Therefore the present distributions should be interpreted as upper limits for the amount of vibrational excitation. In contrast, the LIF technique required knowledge of the predissociative $\text{OH}(^2\Sigma^+)$ excited state and was shown to be susceptible to overestimating the populations of higher rotational levels. The disparity between the chemiluminescence and LIF results can be explained, but still remains to be resolved fully.

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