Resolution test chart showing patterns of vertical and horizontal lines with numerical values: 1.0, 1.1, 1.25, 1.4, 1.6, 1.8, 2.0, 2.2, 2.5, 2.8, 3.2, 3.6, 4.0, 4.5, 5.0, 5.6, 6.3, 7.1, 8.0.

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**The Dynamics in the Reaction of O(1D_g)
With Various Halogenated Methanes**

by

B. I. Niefer, M.Sc.

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
January 22, 1990

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With Various Halogenated Methanes”**

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B. I. Niefer, B.Sc., M.Sc.

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

Chair, Department of Chemistry

Thesis Supervisor

External Examiner

Carleton University
19 March, 1990

Abstract

A multisurface quasiclassical trajectory study of the reaction $O(^1D_g) + H_2(X^1\Sigma_g^+)$ was performed at several initial translational energies ranging between 0.03 and 0.7 eV and for initial rotational quantum states with $J = 0$ or 1. Trajectories were run on both the lowest and next higher eigenvalue surfaces. Trajectories were also carried out on the isotopically substituted reagents HD and D_2 . The potential surfaces for the reaction were obtained from the diatomics-in-molecules method. All of the energetically accessible singlet surfaces were available to each trajectory due to the multisurface nature of the diatomics-in-molecules method. There was general agreement between experimental values and those obtained for trajectories on the lowest eigensurface. Several interesting aspects of the reaction were found for trajectories starting on the eigenvalue 2 surface.

In addition, a study of the reaction of $O(^1D_g)$ with various halogenated methanes was performed by the method of time-resolved Fourier transform infrared spectroscopy to obtain the initial vibrational distributions of the hydrides produced. The reactions studied were:

The OH observed from reaction with CH_3F and CH_3Cl was vibrationally inverted whereas the HF produced in the reactions with CH_3F and $CHClF_2$ and the HCl from reaction with CH_3Cl were hotter than a statistical vibrational distribution. There were indications that the reaction channel that produces an electronically excited carbonyl contributes to these reactions. There was also evidence of secondary reactions contributing to the late-time vibrational distributions. In the reaction with $CHClF_2$ the energetically possible products HCl and OH were not observed within the signal-to-noise of the data.

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I. $O(^1D_g) + H_2$ Trajectory Calculations

I.A. General Description: Trajectory Calculations

I.A.1. Introduction: Trajectory Calculations

The major thrust of this thesis was intended to lie in the results obtained from an experimental investigation of the reaction of $O(^1D_g)$ with various halogenated methanes and the theoretical calculations (for the reactions $O(^1D_g) + H_2$, HD, or D_2) discussed in this section were motivated to provide some insight into interpreting the former set of reactions. By completing an extensive theoretical study, significant insight has been gained, also, in the reaction of $O(^1D_g)$ with H_2 , HD, or D_2 . Both aspects of these results will be presented in this section, with emphasis on the latter. Those results bearing directly on the reaction of $O(^1D_g)$ (hereinafter denoted O^*) with halogenated methanes, although presented in this section, will be more fully discussed in that context in the next section.

Ideally, theoretical calculations for the reaction of O^* with halogenated methanes would be carried out for each individual reaction studied. However, due to the complexity of polyatomic trajectory calculations and the unavailability of potential surfaces for the reactions studied, such an undertaking would be a major work in itself and far beyond the mandate of an experiment-oriented laboratory. Dynamical calculations on the reaction of O^* with H_2 and its isotopic analogs are tractable and will hopefully be a basis for understanding the first set of reactions.

Of particular relevance in this regard are the changes in product distributions when one hydrogen atom is replaced by deuterium. As will be seen in the results of this section,

the mobility of the hydrogen atom (due to its small mass) has a direct bearing on the dynamics of the reaction. The substitution of a deuterium atom for one of the hydrogen atoms gives an indication of the dynamical effects of the relatively massive carbon in the C-H bond.

In the reaction of O^* with a halogenated methane, several reaction channels are energetically accessible. Two of these channels are observable by the technique used in the experimental section of this thesis; elimination of a hydrogen halide and elimination of a hydroxyl radical. This theoretical study is intended to provide insight into the latter channel. There are two dynamical mechanisms by which OH can be formed; direct abstraction and insertion-elimination. Insertion into a C-H bond is the first step required for the displacement of the hydrogen halide also. In addition, the collision complex formed by this insertion corresponds to a stable molecule. This can often lead to the formation of a long-lived intermediate. A long lifetime of the intermediate gives ample time for intramolecular energy relaxation, causing a statistical distribution of the reaction exoergicity into the available rovibrational states of the product molecule(s). The distribution of internal energy (statistical or non-statistical) can often differentiate between the available reaction mechanisms. Recent theoretical and experimental studies of the $O^* + H_2$ reaction, however, have indicated that insertion is the dominant mechanism¹⁻³, that the reaction proceeds via a short-lived intermediate^{2,4,5}, and that it leads to non-statistical rotational and vibrational distributions in the OH product²⁻¹² despite the deep well in the H_2O configuration which is accessed during insertion. The work reported in this thesis bears out these findings, and indicates interesting new aspects - not previously incorporated in trajectory calculations on this reaction - that affect the dynamics of the reaction.

This work is a continuation of the trajectory calculations for the $O^* + H_2$ reaction using similar diatomics-in-molecules (hereinafter denoted as DIM) potential surfaces¹³ and a trajectory program capable of utilizing the full DIM advantage. In particular, all energetically-accessible singlet surfaces with A' symmetry were available to the trajectory program during each trajectory, and the surface on which the trajectory began could be specified. This is particularly important, as will be seen below, since the collinear (O-H-H) surface which correlates directly with the ground state products is slightly higher in energy than the lowest accessible collinear surface and produces a markedly different vibrational distribution when trajectories are constrained to start on it.

I.A.2. The Trajectory Program

The trajectory program was supplied by Dr. P. J. Kuntz and used without modification. The program was quasiclassical in nature and all calculations were carried out using the DIM potential model directly. The formalism for using DIM potentials in trajectory calculations is described in reference 14.

For all trajectories, the initial rovibrational energy was fixed (by specifying the quantum numbers ν and J), as was the initial translational energy T at various values. The other five variables required to specify the initial conditions of the trajectory were chosen quasirandomly from their normal distributions. The range of impact parameters was optimized to give the greatest percentage of reactive trajectories by constraining it to lie between zero and a preset maximum. This value was slightly larger than the maximum value for which reactive trajectories occurred and was determined by running a small set of trajectories for each ν , J , and T initial values.

All trajectories were run with initial vibrational quantum number set to zero. A typical batch for each set of fixed initial conditions (ν , J , T , eigenvalue, molecular reagent) consisted typically of 2700, 3000, or 5000 trajectories. In a few cases, several hundred additional trajectories were run at a slightly higher range of impact parameters to ensure that the cross section (which is related to the highest impact parameter at which reaction occurs) was as well approximated as feasible. The number of trajectories run and highest impact parameter allowed at each set of values is given in table 1. Eig 1 and eig 2 refer to whether the trajectory was started on the lowest or next higher energy surface, respectively, as described in the next sub-section. In all, over 150,000 trajectories were run and analysed.

Table 1: The number of trajectories run (#traj), the number of reactive trajectories of types 2 and 3 (t2, t3), the ratio of type 2 to type 3 (t2 / t3) reactive trajectories, and the maximum reactive impact parameter ($b_{\max}$) for each initial condition. For reactions $O^+ + H_2$, D_2 , types 2 and 3 represent far and near reactions (see text) while for $O^+ + HD$ they represent the products OD and OH respectively. The energy is in eV and the impact parameter $b_{\max}$ is given in bohrs.

J = 0						J = 1				
Energy	#traj	t2	t3	t2/t3	b _{max}	#traj	t2	t3	t2/t3	b _{max}
H ₂ Eig 1										
0.05	500	163	185	0.88	7.0	2700	949	897	1.06	7.18
0.084	5000	1847	1877	0.98	6.57	2700	895	868	1.03	6.52
0.3	5000	2247	1861	1.21	4.84	2700	605	724	0.84	4.90
0.5	5000	2261	1721	1.31	4.32	2700	795	808	0.98	4.29
0.7	5300	2578	1761	1.46	4.06	2700	990	1058	0.98	4.08
H ₂ Eig 2										
0.3	5600	47	905	0.05	2.87	2700	597	226	2.64	2.98
0.4	5600	211	1476	0.14	3.12	-	-	-	-	-
0.5	5600	444	1947	0.27	3.24	2700	527	465	1.13	3.35
0.7	5350	518	1720	0.30	3.43	2700	454	525	0.86	3.44
HD Eig 1										
0.03	2700	1319	856	1.54	8.29	2700	1578	654	2.41	8.23
0.05	2700	1230	779	1.58	7.18	2700	1418	625	2.27	7.29
0.084	2700	1320	788	1.68	6.67	2700	1491	697	2.14	6.65
0.2	2700	1247	738	1.69	5.37	2700	1469	748	1.96	5.67
0.5	2700	1448	664	2.18	4.41	2700	1552	820	1.89	4.49
HD Eig 2										
0.3	3000	537	74	7.26	2.95	3000	570	150	3.80	2.86
0.3	3000	993	219	4.53	3.34	3000	974	305	3.19	3.36
0.7	3000	1084	293	3.70	3.53	3000	1077	334	3.22	3.55
D ₂ Eig 1										
0.03	2700	1011	1094	0.92	7.90	2800	1235	1121	1.10	8.08
0.05	2700	1151	1140	1.01	7.06	2700	1138	1091	1.04	7.24
0.084	2700	1142	1155	0.99	6.43	2700	1135	1193	0.95	6.47
0.2	2700	1172	1110	1.06	5.24	2700	1080	1208	0.89	5.32
0.5	2700	1231	1032	1.19	4.27	2700	1178	1067	1.10	4.24
D ₂ Eig 2										
0.3	3000	8	418	0.02	2.77	3000	206	351	0.59	2.89
0.5	3000	137	955	0.14	3.26	3000	413	736	0.56	3.19
0.7	3000	262	919	0.29	3.31	3000	438	777	0.56	3.34

The equations of motion were written in generalized coordinates and integrated using a fourth order Adams-Moulton predictor-corrector method with a variable step size. At each step the DIM Hamiltonian matrix was diagonalized to obtain the eigenvalues and eigenvectors. The derivatives of the DIM eigenvalues were obtained by use of the Hellmann-Feynmann theorem. All trajectories were started on one of the two lowest adiabatic surfaces (eigenvalue 1 and 2) and with the initial distance between the O^{*}-atom and the centre of mass of the H₂/HD/D₂ molecule set to at least 8 bohrs (1 bohr = 0.5292×10^{-8} cm).

At each step the trajectory was tested for its proximity to a curve crossing, *vide infra*. In the vicinity of a curve crossing a jump was made to the diabatic surface having the largest overlap of its eigenvector with that of the adiabatic eigenvector. The diabatic surfaces were easily obtainable directly from the DIM model. If the trajectory went through a surface intersection, the point of intersection was found and the Landau-Zener formula was used to compute the probability of changing diabatic surfaces. The sequential number of the trajectory was used to seed the random number generator which calculated the Landau-Zener probability to ensure reproducibility of any single trajectory. Once past the region of intersection, the trajectory returned to the adiabatic surface having the largest overlap with the present diabatic eigenvector.

To explore the effect of the H₂O potential well on the dynamics of the reaction, the trajectory was monitored to determine how often it was entered. At each step the trajectory was tested to discern if it had dropped to within 2 eV of the bottom of the well (i.e., if $V < -8.0$ eV). When the potential subsequently attained a value greater than 5 eV above the H₂O minimum, one excursion into the H₂O well was counted. Each such

passage into the H_2O well during the course of the trajectory was monitored and the total listed with the final parameters of the trajectory as the number of times in the well.

There were two ways in which a trajectory could end. When a trajectory had entered and left the strong coupling region (arbitrarily defined as when all the magnitudes of the vectors between the atoms were less than preset values, i.e. $R(\text{OH}) < 4$ bohrs and $R(\text{H}_2) < 4.5$ bohrs), it was terminated and all relevant final parameters were calculated and tabulated. If the trajectory was still in the strong coupling region after it had run for a preset length of time, it was terminated without calculation of final parameters and these trajectories were not used in the analysis of the batch. Those trajectories that ended normally were assigned as belonging to one of three types, depending on whether the atomic species at the end of the trajectory was the O^* -atom (indicating a non-reactive trajectory), the H/D-atom (for H_2/D_2) that had been closest to the O^* -atom at the beginning of the trajectory, or the H/D-atom (for H_2/D_2) furthest from the O^* -atom at the beginning of the trajectory. These were denoted as types 1, 2, and 3 respectively. The $\text{O}^* + \text{HD}$ trajectories required a slightly different definition of types 2 and 3 due to the expanded range of the initial azimuthal angle; the loss of symmetry when the molecule is composed of unlike atoms required that the azimuthal angle be sampled from 0 - 180° rather than 0 - 90° . As a result, types 2 and 3 denoted the products OD and OH respectively. Collisional deactivation of the $\text{O}(^1\text{D}_g)$ to $\text{O}(^3\text{P})$ was not a possible channel for this trajectory study since the DIM model used in these calculations contained only singlet surfaces. The triplet surfaces (and the singlet surfaces with A'' symmetry) were intentionally removed from the model to increase computation speed; since they were not used at this stage of the trajectory study, this was considered a prudent strategy.

At the end of each normal trajectory, energy conservation was checked (the use of diabatic surfaces often incurred some nonconservation), and if the final energy differed from the initial value by more than a preset amount, the trajectory was rerun using a smaller initial step size. The final rovibrational quantum state was determined, as were several other final state values, and forty-nine initial and final parameters for each trajectory were listed in an output file for later analysis.

The trajectories were computed using four different systems; an IBM 370 at the National Research Council of Canada (Computing Services), a Floating Point Systems processor attached to the IBM 370, a SUN3 workstation and the SUN3 workstation with a floating point accelerator board attached. Due to the relatively small size of the DIM model used, it was found that these *multi-surface* calculations were competitive in terms of computation time with other *single* surface trajectory programs.

I.A.3. The DIM Surfaces

The DIM model used was supplied by P. J. Kuntz. It is essentially the same as what is called Model B in references 15 and 16; only the long-range behaviour of the $\text{OH}(^2\Sigma^+)$ curve has been modified in order to better reproduce the experimental rate constant. Its basic structure and those features relevant to this study will be given below.

There are five valence-bond structures contributing to the model:

Structures *i* and *v* each have one basis function associated with them, structure *ii* has three, and structures *iii* and *iv* each have two for a total of nine basis functions. This gives a 9×9 DIM Hamiltonian **B** matrix that is diagonalized at each step in the trajectory program. The algebra by which the **B** matrix is constructed from the individual atomic and diatomic fragment matrices and a listing of the diatomic fragments required are given in reference 15. The adjustments (excluding the single additional modification mentioned previously) made to the individual diatomic fragment matrices to fit the model to experimental and *ab initio* values is given in reference 16 and the adjustment procedure is outlined in reference 17.

The energies and correlations for the low lying states at selected geometries relevant to the present calculations are given in figure 1. For all states, the zero of energy corresponds to the infinitely separated atoms in their ground states: $\text{O}(^3\text{P}) + \text{H} + \text{H}$. Important points of energy and geometry for the surfaces are given in table 2. In

Table 2: The values of the more important features of the potential surface used in this study. Energies are in eV (relative to $O(^3P) + H + H$), frequencies in cm^{-1} and distances in bohr. Experimentally determined values are given in the right-hand column. Those in brackets represent values the model was specifically designed to reproduce.

Feature	DIM Potential Value	Exp. Value
$O^* + H_2$ channel energy	-2.780 @ $R_{HH}=1.4015$	-2.784
$\omega_e(H_2)$	4339.78	4403.57
$H + OH(X^2\Pi)$ channel energy	-4.620 @ $R_{OH}=1.8337$	-4.63
$\omega_e(OH(X^2\Pi))$	3909.27	3735.21
$H + OH(A^2\Sigma)$ channel energy	-0.562 @ $R_{OH}=1.9015$	-0.58
$H_2O(X^1A_1)$ minimum energy	-9.869 @ $R_{OH}=1.8870, R_{HH}=2.9315$	(-10.07)
$H_2O C_{2v}$ barrier to insertion	none	(none)
$H_2O C_{2v}$ barrier to inversion	-8.519 @ $R_{OH}=1.8594, R_{HH}=3.6791$	
$H_2O(X^1A_1)$ angle at minimum	101.93°	(104.5°)
$H_2O(2^1A_1)$ @ $H_2O(X^1A_1)$ minimum	2.142	(-0.35)
$H_2O(1^1B_1)$ @ $H_2O(X^1A_1)$ minimum	2.445	(1.0)
$HOH(^1\Sigma_g^+)$ minimum energy	-8.519 @ $R_{OH}=1.8595$	(-8.34)
$HOH(^1\Pi_u)$ saddle energy	-4.426 @ $R_{OH}=2.1103$	
$OHH(^1\Sigma)$ minimum energy	-3.407 @ $R_{OH}=1.9091, R_{HH}=1.7274$	
$OHH(^1\Pi)$ barrier energy	-2.621 @ $R_{OH}=3.1726, R_{HH}=1.4253$	-2.63

addition, certain significant features of the surfaces are presented as contour diagrams in figures 2, 3, and 4.

The basic model was constructed to reproduce six features of the $O^* + H_2$ system. The target values are listed in the right hand column of table 2. Even though not all features were accurately attained (of particular importance the depth of the H_2O well and the H-O-H angle at this minimum in the C_{2v} geometry), the differences between the target value and those realized in this model were not considered to seriously detract from it. The two features considered to be of greatest importance in the trajectory calculation, no barrier to insertion on the C_{2v} and H-O-H lowest surfaces (the first eigenvalue) and the height of the barrier for the O-H-H $^1\Pi$ abstraction surface (the second eigenvalue), were accurate.

Figure 2 depicts the insertion pathway via C_{2v} configurations from reactants (at the right of the plot) through the deep H_2O minimum to collinear H-O-H (at the left of the plot). Even though the contours in this figure are not dense enough to illustrate the lack of a barrier in the entrance channel, a study of a cut through the surface at an H_2 separation of 1.4015 bohrs (the H_2 equilibrium separation in this model) showed that there were a few minor undulations in the potential (less than 0.002 eV in the vicinity of $R_{O-HH} = 5.5$ bohrs) but no barrier existed. Most of the deficiencies in this model are apparent in this figure. The depth and location of the H_2O minimum, as stated earlier, do not exactly match the expected values and there is a small 'barrier' to inversion (approximately 0.023 eV above the H-O-H insertion minimum) at $R = 0.27$ bohrs and $R_H = 3.68$ bohrs. This barrier to inversion is very small, well below the reagent energy, and should not significantly affect the trajectories.

BH201P15 H--O--H C_{2v} GEOMETRY EIG 1

Figure 2: Potential energy contours for the lowest singlet eigenstate of the H₂O (C_{2v}) insertion. Energies are in eV and distances in bohr.

Inspection of figure 1 (depicting the energy levels of the relevant surfaces at various symmetry configurations) illustrates that reaction on the lowest *eigenvalue* for either collinear insertion or collinear abstraction leads directly to products. However, for either of these geometries, the *surface* must be changed to reach the ground state OH product. In the collinear insertion geometry ($D_{\infty h}$ symmetry), the ground ($^1\Sigma_g^+$) state does not correlate with the ground state of the separated products ($OH(X^2\Pi) + H(^2S)$) but with the first excited state ($OH(A^2\Sigma^+) + H(^2S)$). Rather, it is the first excited ($^1\Pi_u$) state of the collinear insertion geometry that correlates to the ground state of the products. Therefore, any trajectory that proceeded on the lowest eigenvalue ($^1\Sigma_g^+$ in the entrance channel) by an insertion mechanism went through a conical intersection between the $^1\Sigma_g^+$ and $^1\Pi_u$ surfaces and had to switch to the $^1\Pi_u$ surface in order to form the products in their ground state.

The two lowest collinear insertion surfaces and their intersection are depicted in figure 3. Both channels represent exit channels for this reaction: the entrance channel cannot be depicted on a two dimensional contour plot for O^* insertion. The lowest *eigenvalue* is given by the solid contours, the second *eigenvalue* is given by the dashed contours and their intersection is indicated by the thick dashed line. For all values of R_{O-H} to the right or above the intersection, the solid contours are for the $^1\Sigma_g^+$ state, while the dashed contours are for the $^1\Pi_u$ state. To the left or below the intersection, the surfaces are reversed; the solid contours are for the $^1\Pi_u$ state. This intersection persisted as an energetically accessible avoided crossing for a small range of H-O-H angles ($\pm 10^\circ$ about the 180° collinear geometry) and affected any trajectories with near-collinear insertion geometries as the products separated. The small increase in the potential around the intersection did not act as a bottleneck since the intersection occurred for a wide range of internuclear distances at energies well below the energy of the reagents. The major effect

Figure 3: Potential energy contours for the two lowest singlet eigenstates of the HOH ($D_{\infty h}$) collinear insertion. The solid contours always shows the lowest energy eigenvalue, the dashed contours the second energy eigenvalue, and their intersection by the thick dashed line. Energies are in eV and distances in bohr.

of the intersection on the trajectories was to delay formation of the product if the trajectory remained on the 'wrong' surface ($^1\Sigma_g^+$) after the intersection thus increasing the lifetime of the collision complex.

The collinear abstraction mechanism also required a surface crossing for the formation of ground state products as seen in figure 1. In the entrance channel of this symmetry configuration, three surfaces ($^1\Sigma^+$, $^1\Pi$, and $^1\Delta$) are degenerate. As the O^* -atom approaches the H_2 molecule this degeneracy lifts. In this DIM model, in the entrance channel the $^1\Sigma^+$ surface is attractive, the $^1\Pi$ surface rises slightly to a small barrier before it too becomes attractive, and the $^1\Delta$ surface is repulsive. However, only the $^1\Pi$ surface remains attractive in the exit channel and correlates with the ground state ($OH(X^2\Pi) + H(^2S)$) products. This requires that any trajectory entering the exit channel on the lowest eigenvalue in this configuration must change surfaces ($^1\Sigma^+$ to $^1\Pi$) in order to form products. This curve-crossing can be seen in figure 4. Again, the lowest *eigenvalue* is depicted by the solid contours, the second *eigenvalue* is given by the dashed contours, and their intersection is depicted by the thick dashed line. Below the intersection, the solid contours refer to the $^1\Sigma^+$ surface and the dashed contours to the $^1\Pi$ surface. Above the intersection, the surfaces are reversed; the solid contours are for the $^1\Pi$ surface. As can be seen in this figure, the intersection is restricted to the exit channel.

This intersection has two effects on trajectories. It can delay the formation of products in trajectories starting on the *first* eigenvalue that approach the exit channel in a collinear O-H-H geometry and do *not* switch to the $^1\Pi$ surface at the intersection. In addition, those trajectories that begin on the *second* eigenvalue (for collinear abstraction this requires only about 0.16 eV above the reagent channel energy as given in table 2) can also be delayed if it *does* switch surfaces at this intersection and remains as the second

BH201P15 O--H-H 180 DEGREES EIG 1 ———

BH201P15 O--H-H 180 DEGREES EIG 2
 BH201P15 O--H-H 180 DEGREES EIG 2 - - - - -

Figure 4: Potential energy contours for the two lowest singlet eigenstates of the OHH ($C_{\infty v}$) collinear abstraction. The solid contours always shows the lowest energy eigenvalue, the dashed contours the second energy eigenvalue, and their intersection by the thick dashed line. Energies are in eV and distances in bohr.

eigenvalue. For these latter trajectories, formation of products can be delayed even if it does succeed in changing to the lower surface at the intersection since the rapidly changing geometry of the collision can cause it to reform a collision complex and even access the deep H_2O well. Thus a simple abstraction (the energetically necessary mechanism for eigenvalue 2 trajectories at the reagent energies used in this study) can become a complex insertion. As in the case of insertion, the O-H-H intersection is not limited to the collinear case; an energetically accessible avoided crossing extends to geometries where the O-H-H angle is as much as 30° from collinear. This large range of geometries causes the abstraction intersection to be more important than the corresponding one for insertion, although neither occurred with great frequency for trajectories that started on eigenvalue 1. Typically, only around 10% of all eigenvalue 1 trajectories were ever sufficiently close to an intersection to switch to diabatic mode, and about 80% of these occurrences were for the O-H-H intersection.

Several sample trajectories are depicted in figures 5, 6, and 7 to illustrate these points. These trajectories were chosen to display certain aspects and are not meant to illustrate limiting cases. All trajectories underwent unique motions, which were occasionally quite complex, although some aspects were similar in a large number of trajectories. All depicted trajectories were for the reaction $\text{O}^* + \text{H}_2$ with the vibrational and rotational quantum numbers set to zero. In figures 5 and 6, the kinetic energy and beginning eigenvalue (denoted as 'Eig') are listed on each trajectory. The three internuclear distances in bohrs (positive y-axis) and the potential in eV (negative y-axis) are given as a function of the length of time in program time units (each program time unit $\approx 4.14 \times 10^{-15}$ seconds) that the trajectory has been propagating. The eigenvalue ('1' or '2') and the mode (adiabatic 'A' or diabatic 'D') are given just above the time axis;

Figure 5: Plot of the three internuclear distances and the potential energy as a function of time for trajectories starting with eigenvalue 1. The internuclear distances R_{HH} , R_{OH_1} , and R_{OH_2} (in bohr) are on the positive y-axis and the potential energy (in eV) on the negative y-axis. The time, given in program time units, is on the x-axis. (a) A typical eigenvalue 1 trajectory. (b) A trajectory which changed eigenvalues at an intersection.

Figure 6: Plot of the three internuclear distances and the potential energy as a function of time for trajectories starting with eigenvalue 2. The internuclear distances R_{HH} , R_{OH1} , and R_{OH2} (in bohr) are on the positive y-axis and the potential energy (in eV) on the negative y-axis. The time, given in program time units, is on the x-axis. (a) A typical eigenvalue 2 trajectory. (b) A trajectory which underwent insertion.

whenever one (or both) of these changes it is so indicated at the appropriate point of the trajectory.

The trajectory in figure 5 (a) represents a typical progression for trajectories starting on the lowest (eigenvalue 1) surface; at least one excursion into the deep H_2O well ('Well 1' in the trajectory legend) and at no time was it adequately close to a surface intersection to switch to diabatic mode (remained on surface A1; adiabatic with eigenvalue 1). The final vibrational level was low (' ν Final 0') and the final rotational level was reasonably high ('J Final 31'); each agreeing with the peaks of their respective distributions which are presented in a subsequent section. The trajectory in figure 5 (b) depicts some of the points discussed previously in this section. It starts on the lowest eigenvalue surface (A1) and approaches the intersection in abstraction geometry, around time unit nineteen, at which point it switches to the diabatic surface with eigenvalue 1 (D1). As it goes through the intersection, it switches *eigenvalue* (D2) thus remaining on the same *surface*. However, at the low energy of this trajectory it is confined to a region of phase space close to the intersection and cannot proceed into the exit channel or return to the entrance channel with eigenvalue 2. Finally, at time unit twenty-two and a half it again finds the abstraction intersection and returns to eigenvalue 1. However, it is no longer propagating along the exit channel but instead returns to again form a collision complex which accesses the deep H_2O well before finally finding an exit channel to become products. From the trajectory in figure 5 (b), it is easily seen that the intersections can cause complications and serve to lengthen the duration of the collision.

Figure 6 is for trajectories that started on the second eigenvalue. Again, the trajectory in (a) represents a typical eigenvalue 2 trajectory. It proceeds by an abstraction type geometry until it nears the intersection in the exit channel at time unit fourteen at which

point it switches to diabatic mode with eigenvalue 2 (D2). At the intersection it changes *eigenvalue* (thus remaining on the same *surface*) and switches back to adiabatic mode with eigenvalue 1 (A1) as it leaves the vicinity of the intersection. It then continues along the exit channel to form products. The final vibrational level is three, consistent with the high vibrational energy expected from a $\text{H} + \text{LL}$ abstraction reaction on an attractive potential surface¹⁸ and the rotational level is reasonably low, each consistent with their distributions which are presented in a subsequent section. The trajectory in figure 6 (b) also starts on eigenvalue 2 and displays the complications that can arise from the intersections. At time unit thirteen and a half it nears the intersection and makes a successful crossing to the lower eigenvalue. However, the motions of the atoms are such that it is no longer progressing along the exit channel but returns to again form a collision complex, uneventfully approaches the insertion intersection around time unit eighteen, and then enters the deep H_2O well before it again locates an exit channel. Thus, from the second trajectory in each figure it is seen that having two surfaces accessible to the trajectories at all times coupled with their intersections leads to more complex trajectories in which the dynamics are not straightforward.

As stated previously, insertion is considered to be the dominant mechanism for this reaction at moderate temperatures¹⁻³, which is consistent with the trajectories in this study starting on eigenvalue 1. This is due to the high mobility of the H-atom (resulting from its small mass) and the large impulses expected as the complex approaches the deep H_2O well during insertion. These effects can be seen in the trajectory depicted in figure 7. The trajectory was constrained to be nearly 'end-on', that is, its initial geometry was at most 10° from being a collinear O-H-H approach. In part (a) of the figure, the cartesian coordinates of the three atoms are depicted at subsequent times in the trajectory on a 3-dimensional set of axes and in part (b) the potential and internuclear distances for

KINETIC ENERGY=0.084 SURFACE 1 TRAJECTORY 4

Figure 7: Depiction of a nearly 'end-on' trajectory on the eigenvalue 1 surface. The O^* -atom initially made an angle of 10° to the H_2 bond. (a) A plot of the cartesian coordinates of the three atoms at subsequent times. The x coordinate of each atom is incremented a fixed amount between each 'snap-shot'. The position of the O^* -atom is given by the solid line connecting the two O's. The positions of the two H-atoms are given at equally spaced intervals by the dashed and dotted lines, the heights of which depict their distance from the 'observer'. The two H-atoms are periodically connected by lines to the same temporal point on the O^* -atom curve.

Figure 7 continued: (b) Plot of the three internuclear distances and the potential energy as a function of time for the trajectory given in part (a) of this figure. The internuclear distances R_{HH} , $R_{\text{OH}1}$, and $R_{\text{OH}2}$ (in bohr) are on the positive y-axis and the potential energy (in eV) on the negative y-axis. The time, given in program time units, is on the x-axis.

the same trajectory are given following the convention described for figures 5 and 6. The x coordinate in part (a) is incremented a fixed amount between each 'snap-shot' so the individual motions can be easily followed. The motion of the O^{*}-atom is depicted during the entire trajectory by the solid line connecting the two 'O's at either end of the figure. The positions of the two H-atoms are given at equally spaced intervals by the series of dashed and dotted horizontal lines. The relative heights of these lines represent their distance from the 'observer' (positioned about midway up the z-axis, near the end of the x-axis and some distance in the negative y direction). This assists in observing differences in the Y coordinates of the two H-atoms. To aid in following the sequence of the trajectory, the two H-atoms are periodically connected by lines to the same temporal point on the O^{*}-atom curve. At time zero the trajectory begins with the O^{*} atom directed towards one end of the H₂ molecule. There is little change in orientation of the H₂ molecule as the trajectory progresses and it is approached by the O^{*}-atom. At approximately time unit ten in part (b) of the figure the potential begins to change rapidly resulting in the separation of the H-atoms (the complex goes from near-collinear O-H-H to H-O-H in the approximately two program time units between the 20'th and 25'th 'snap-shots' in part (a) of the figure). As a result of the rapid re-orientation of the H₂ molecule, the resulting product is left with greater than statistical rotational energy. The asymmetric stretch induced in the H₂O complex as it is formed in this re-orientation leads to greater than expected vibrational energy in the product also. All three results, insertion, product rotation, and product vibration, are all due to the ability of the H₂ molecule to rapidly re-orient itself under the influence of the large impulses derived from the steep insertion potential.

I.B. Results: Trajectory Calculations

I.B.1. Introduction: Trajectory Results

The majority of the results from the trajectory calculations are given as histogram plots. The output file for each set of initial conditions, containing forty nine initial and final parameters for each trajectory, was analysed to give distributions (normalized to unity) for the parameters of interest. In addition, a limited number of double-variable distributions were calculated to explore correlation between two specific parameters. The initial conditions are listed on most of the figures. Unless otherwise amended, the five initial conditions are $O^* + H_2$, $v = 0$, $J = 0$, eigenvalue 1 and initial kinetic energy $(T) = 0.084$ eV.

The histograms are typically plotted as $P(x)$ versus x where $P(x)$ is the distribution of parameter x and the peak of the distribution is normalized to unity. The distributions for the impact parameter and initial azimuthal angle have been adjusted for their proper Monte Carlo selection. This necessitated that the value for the bin with x between i and $i+1$ was divided by $(b_{i+1}^2 - b_i^2)$ for the impact parameter or by $(\cos(a_i) - \cos(a_{i+1}))$ for the initial azimuthal angle. Double variable histograms are a plot of $P_n(x)$ versus x for various values, n , of the second parameter. The name and value of the second parameter are listed in each panel of the double variable histograms. These histograms are normalized so the peak of the entire distribution is unity and, as a result, the peak for any one $P_n(x)$ distribution is usually less than unity.

I.B.2. Effects of Various Initial Conditions

I.B.2.a. Initial Eigenvalue

This DIM model has several surfaces simultaneously available to all trajectories, as described in sub-section I.A.3. The two lowest surfaces are of greatest importance since for collinear geometries only the second surface in the entrance channel correlates with the ground state products, $\text{OH}(X^2\Pi) + \text{H}(^2\text{S})$, in the exit channel. In addition, any trajectory with sufficient energy can propagate entirely on the second surface thus, typically, avoiding the deep H_2O well. Reaction on these two surfaces, as expected from their grossly different properties, proceed by different mechanisms and are associated with widely differing initial and final state distributions. Some of the more important differences in the distributions resulting from reaction on these two surfaces are depicted in figures 8 to 13 (in each of the histogram plots only the top two panels are discussed in this sub-section, the remaining panels are discussed in the next sub-section).

The distribution of impact parameters that lead to reaction is given in figure 8. The top, left-hand panel is for trajectories that started with eigenvalue 1 and 0.084 eV of translational energy, while the right-hand panel is for trajectories that started with eigenvalue 2 and 0.3 eV of translational energy. The latter trajectories required more translational energy for reaction because of the presence of a barrier (~ 0.16 eV) in the entrance channel on the $^1\Pi$ collinear O-H-H abstraction surface. The eigenvalue 1 distribution was essentially flat over most of the range of contributing impact parameters after which it dropped rather rapidly to its final value (around 6.5 bohrs). The probability for reaction between 0 and 5.75 bohrs was in actuality approximately equal to one over this entire range of impact parameters as indicated by the high reactivity: of all the trajectories in this impact range, over 97.5% were reactive. This distribution closely

Figure 8: Histogram plot of the reactive impact parameter distributions for the reaction $O^* + H_2$ and trajectories starting with $J = 0$ and eigenvalue 1 (Eig 1) or eigenvalue 2 (Eig 2). The initial translational energy (T in eV) is given in each panel.

approximated a unit step function. An opacity function of this form is what is expected from a 'billiard-ball' model in which there is no steric hindrance to reaction¹⁹ and would not normally be considered consistent with an insertion mechanism of reaction. However, the mobility of the H-atoms counteracted any steric effect typically associated with insertion reactions, and produced this essentially flat distribution.

The eigenvalue 2 distribution peaked at zero impact parameter and gradually decreased from there to its final value (around 2.75 bohrs). The shape of this distribution and the fact that the largest reactive impact parameter was much smaller than that for trajectories starting with eigenvalue 1 indicated that a rather severe steric hindrance was operative in reaction under these initial conditions. As previously discussed, trajectories that started with eigenvalue 2 proceeded, typically, by abstraction. The distribution of impact parameters was consistent with this mechanism, although, by itself, it did not differentiate between abstraction or insertion.

The histogram plots for the number of times the H₂O well was accessed are given in figure 9. An excursion into the H₂O well was defined as whenever the potential had dropped to less than -8 eV and subsequently reached a value above -5 eV. Again, the upper left panel is for eigenvalue 1 and 0.084 eV of translational energy while the upper right panel is for eigenvalue 2 and 0.3 eV. The left panel in this figure clearly indicates that the majority of trajectories starting on eigenvalue 2 do not access the deep H₂O well: the distribution is sharply peaked at 0 times in the well. This is consistent with the energy levels presented in figure 1 and the potential surfaces in figure 4. Trajectories that start with eigenvalue 2 are energetically constrained to remain in a nearly collinear abstraction geometry (due to the rapid rise in the eigenvalue 2 potential with angle of approach) until they reach the exit channel where they must go through the intersection

Figure 9: Histogram plot of the number of times the average trajectory entered the H_2O well for the reaction $O^* + H_2$ and trajectories starting with $J = 0$ and eigenvalue 1 (Eig 1) or eigenvalue 2 (Eig 2). The initial translational energy (T in eV) is given in each panel.

and cross to the lower eigenvalue. From figure 9, approximately 15% of the trajectories return to enter the well, thus turning, what is normally a direct abstraction into a complex insertion. The percentage of trajectories that return to again form a collision complex after changing eigenvalue at the intersection without entering the well before forming products is unknown as they are grouped in with those that underwent a direct reaction. They are expected to contribute very little to the $\text{Well} = 0$ value based on the percentage of eigenvalue 1 trajectories that react without accessing the well (see below).

Of the trajectories that start on eigenvalue 1 (figure 9, top left panel), less than 4% form products without accessing the H_2O well. The majority of these trajectories enter the well at least once (25% make only one trip into the well) and many oscillate within the well several times before exiting. Those trajectories that do access the well several times lose all attributes of a direct reaction and can be loosely described in terms of unimolecular dissociation.

One attribute of unimolecular dissociation that can be ascribed to these trajectories is the existence of a decay rate for the collision complex. This is illustrated in figure 10, a semi-log plot of the distribution of the number of times the trajectory accessed the well. A population that follows a first order decay decreases exponentially with time. A semi-log plot of the population as a function of time produces a straight line with the slope equal to the negative of the decay constant. This concept can be applied to the distribution for the number of times in the well. For each set of initial conditions an average time between successive excursions into the well can be determined thus relating the number times in the well to the time elapsed since the collision complex formed. Similarly, the value of the distribution at each 'times in the well' represents the remaining population of the collision complex at that time. A semi-log plot of the

$O(^1D) + H_2$ Trajectories, Eig 1

Figure 10: Semi-log plot of the distribution of times in the well versus times in the well for the reaction $O(^1D) + H_2$ starting with eigenvalue 1 and $J = 0$. The two lines represent the best straight line fit to the points for 2 or more times in the well.

distribution as a function of times in the well produced a linear plot for two or more times in the well (figure 10) which indicated that for trajectories accessing the well two or more times the collision complex followed first order decay. Trajectories entering the well zero or one times did not lie on the line and will be termed as 'direct'. The analysis of the two lines plotted on this figure will be given in the next sub-section.

The vibrational distributions from the eigenvalue 1 and 2 trajectories are given in figure 11. The eigenvalue 1 results have a monotonically decreasing distribution from $v' = 0$ (the most probable) to the maximum attainable level, $v' = 5$. This is consistent with an insertion mechanism in which a long-lived complex is formed and the reaction exoergicity is statistically distributed amongst the available internal states. However, the calculated distribution is somewhat 'hotter' (greater distribution in the higher levels) than a statistical distribution (see appendix A.1) due to the direct reactions that entered the well zero or one times (approximately 29% of the trajectories). Analogously, the eigenvalue 2 distribution is inverted, peaking in $v' = 4$ as a result of its direct (predominantly abstraction) mechanism (96% entered the well zero or one times).

The rotational distributions are presented in figure 12. Both distributions (for eigenvalue 1 and 2) appeared hotter than statistically expected if they were the result of a long-lived complex, peaking at $J' = 21$ at 0.084 eV rather than the statistically expected $J' = 16$. Neither of these distributions were consistent with their expected mechanisms. Eigenvalue 1 trajectories with their large component of long-lived collision complexes would be expected to have a distribution more closely approximating a statistical one. Eigenvalue 2 trajectories, with a predominantly direct collinear abstraction mechanism, would not be expected to have a statistical distribution but would be expected to peak at much lower J' values consistent with the small collisional angular momentum resulting

Figure 11: Histogram plot of the vibrational distributions for the reaction $O^* + H_2$ and trajectories starting with $J = 0$ and eigenvalue 1 (Eig 1) or eigenvalue 2 (Eig 2). The initial translational energy (T in eV) is given in each panel.

Figure 12: Histogram plot of the rotational distributions for the reaction $O^* + H_2$ and trajectories starting with $J = 0$ and eigenvalue 1 (Eig 1) or eigenvalue 2 (Eig 2). The initial translational energy (T in eV) is given in each panel.

Figure 13: Histogram plot of the centre-of-mass scattering angle distributions for the reaction $O^* + H_2$ and trajectories starting with $J=0$ and eigenvalue 1 (Eig 1) and eigenvalue 2 (Eig 2). The initial translational energy (T in eV) is given in each panel.

from their small impact parameters. The peak at large J' values was completely inconsistent with what was expected for an abstraction mechanism.

The distribution of centre-of-mass scattering angle (figure 13) for eigenvalue 2 trajectories was as expected for a direct abstraction reaction; the molecular product is predominantly scattered in the backward direction. The eigenvalue 1 distribution shows apparent forward-backward scattering overlaying a flat distribution. The flat component in the eigenvalue 1 distribution resulted from those trajectories that formed a long-lived complex whereas the forward-backward peaks were due to the direct reactions which entered the well at most one time. When the average value of the flat background was subtracted from the distributions between 0 to 40° and 150 to 180°, the remainder represented 27% of the trajectories which agreed well with the number that entered the well at most once (29%). The forward-backward symmetry was the result of the equivalence of the two H-atoms; either O-H bond in the H-O-H intermediate had nearly equal probability of breaking, as will be seen in a subsequent sub-section.

I.B.2.b. Initial Energy, Translational or Rotational

I.B.2.b.i. Initial Translational Energy

Figures 8 to 13 illustrate the major effects that the initial translational energy had on the trajectories. The four panels on the left-hand side of each histogram plot are for trajectories that started with eigenvalue 1 and initial translational energy of $T = 0.084$ (top), 0.3, 0.5, and 0.7 eV (bottom). The four panels on the right-hand side are for trajectories that started with eigenvalue 2 and initial translational energies of $T = 0.3$ (top), 0.4, 0.5, and 0.7 eV (bottom). The initial translational energy had little effect on trajectories starting with eigenvalue 1; only the maximum impact parameter (figure 8)

decreased with increasing translational energy as expected: for reactions without a barrier, the cross section which is directly related to the maximum reactive impact parameter, decreases with increasing translational energy¹⁹. In fact, the value of the maximum impact parameter (listed in table 1) decreased approximately as $T^{-1/6}$ which is the expected dependence from the long-range potential between an atom and a diatomic molecule¹⁹.

The maximum impact parameter for trajectories that started with eigenvalue 2 increased with increasing initial translational energy. This behaviour was expected since there was a barrier to reaction for these trajectories¹⁹. The shape of the distribution (figure 8) also changed with translational energy. At $T = 0.7$ eV, the distribution no longer peaked at 0 bohr but had a broad peak centered around 1.5 bohrs. An abstraction mechanism could not account for this shifted peak. In addition, the increase in the number of long-lived insertions at the higher energy (*vide infra*) was not sufficient to account for this shift in the peak. The possibility of a third mechanism contributing to reaction at higher energies for eigenvalue 2 trajectories was suggested.

The shape of the distributions for the number of times in the well (figure 9) for trajectories with eigenvalue 1 changed very little as the initial translational energy increased. The only significant change was the number of direct (entering the well 0 or 1 times) reactions. These increased from 29% at 0.084 eV to 46% at 0.7 eV. The only other significant change was the characteristic decay rates of those trajectories that formed a complex. From figure 10, the slopes of the two lines differ. The slopes were 0.368 and 0.540 for $T = 0.084$ and 0.7 eV respectively. The magnitudes and, in particular, the ratio of these slopes ($\text{slope}(0.7) / \text{slope}(0.084) = 1.47$) were well

approximated by the unimolecular decay rate when an RRK model of the transition state was assumed¹⁹.

When the complex decayed to products, it could do so from almost any configuration. From the potential curves, for most configurations there was a slight 'barrier' as the products entered the exit channel. For the extreme cases of the collinear surfaces, this 'barrier' occurred at the intersection of the two surfaces. Since the near-intersection persisted for rather large angles from collinear, its effect on the surfaces also persisted and a slight 'barrier' was present for most configurations. For a collision complex with a barrier in the exit channel, its decay rate is given by¹⁹:

$$k' = \bar{\nu} (E_a'/U)^{s-1} \quad 1$$

where, $\bar{\nu}$ is an average vibrational frequency of the complex and s is the number of normal vibrational modes in the complex (for H_2O $s = 3$). E_a' is the energy available for partitioning at the exit barrier and U is the total energy measured from the ground state of the complex. Analysis of the vibrational structure of the complex and the exit transition state is beyond the requirements of this rough calculation and the channel energies of these two configurations will be used instead of their ground state energies. In addition, the average vibrational frequency of the complex will be approximated as equal to the average frequency for successive excursions into the well for each set of initial conditions. The 'barrier' height in the exit channel had a wide range of values since any configuration was possible just prior to entering the exit channel; 0.017 eV for collinear insertion and 1.251 eV for collinear abstraction and undetermined values for geometries in between. The H_2O complex formed in most trajectories was trapped in the bending mode undergoing repeated inversion of the complex until the exit channel was finally entered. As a result, the insertion 'barrier' was a much better approximation for this

calculation than the abstraction 'barrier'. This value for the 'barrier' gave calculated values for the decay constant of $4.4 \times 10^{12} \text{ s}^{-1}$ for $T = 0.084 \text{ eV}$ and $7.1 \times 10^{12} \text{ s}^{-1}$ for $T = 0.7 \text{ eV}$ with a ratio $k'(0.7)/k'(0.084) = 1.6$. This ratio was very close to the ratio of the slopes given previously (1.47) for the lines in figure 10. The linearity of the lines in figure 10 and the good agreement between theory and measurement for the ratio of their slopes strongly suggests that those trajectories entering the well two or more times could be described as undergoing unimolecular dissociation.

The distribution of times in the well for trajectories starting with eigenvalue 2 changed very little in overall shape as the initial translational energy increased. For these trajectories, the number of reactions that formed a long-lived complex (accessed the well 2 or more times) increased from 4% at 0.3 eV to 13% at 0.7 eV.

The distribution of the vibrational levels, figure 11, for trajectories that started with eigenvalue 1 reflected the increase in direct reactions as the initial translational energy was increased. The distributions were less statistical as the translational energy increased and at 0.7 eV the vibrational distribution was inverted. Even though the vibrational distributions were 'hotter' as the initial translational energy increased, the fraction of the exoergicity channeled into vibration remained almost constant at 0.38 for all the initial energies used in this study. Direct insertions produced high vibrational excitation of the product molecule because the asymmetric stretch mode of the H-O-H intermediate was excited as the H_2 swung around to facilitate insertion. This was clearly seen in the trajectory plotted in figure 7.

The vibrational distributions for trajectories that started with eigenvalue 2 became less inverted as the initial translational energy increased and the fraction of the reaction exoergicity that was channeled into vibration dropped from $f_{\text{vib}} = 0.49$ at 0.3 eV to 0.41 at

0.7 eV. This behaviour was opposite to that expected if abstraction remained as the only mechanism of reaction: increased translational energy would be channeled into increased vibrational excitation for abstraction in a $H + LL$ reaction on an attractive potential surface¹⁸. Again, the increase in trajectories forming a long-lived complex could not account for this relatively large change in the distribution.

The rotational distributions from eigenvalue 1 trajectories (figure 12) became colder as the initial translational energy increased, which may have reflected the increased number of direct reactions which channeled a greater fraction of the reaction exoergicity into vibration leaving less for rotation. The eigenvalue 2 rotational distributions noticeably changed shape as the energy increased. For the eigenvalue 2 trajectories at 0.7 eV the distribution appeared to have two distinct contributions, one at very low J' values (peaking around 5) and another at higher J' values (peaking around 24). The latter peak was assigned to the abstraction reactions and the increased number of reactions that formed a long-lived complex (which preferentially populates the higher rotational levels). The low- J' peak could not be accounted for; if a stripping mechanism were to become active at this energy or a more bent reaction geometry was possible, they would be expected to produce high rotation.

The scattering angle distribution (figure 13) for eigenvalue 1 became more peaked in the forward-backward directions. This, again, was consistent with the increase in direct reactions. The eigenvalue 2 distributions changed from backwards peaking at 0.3 eV to almost flat with a slight forward peak at 0.7 eV. This extreme change in the scattering angle distribution could not be accounted for by the (relatively) small increase in reactions that formed a long-lived complex.

1.B.2.b.ii. Initial Rotational Energy

The trajectories for all initial conditions (translational energy, initial eigenvalue and isotope) were run for initial rotational quantum numbers $J = 0$, and 1 (the rotational levels with the greatest populations for H_2 at 300 K). Figures 14, 15, and 16 depict the distributions of impact parameter, final v' level, and scattering angle, respectively, for the reaction $O^* + H_2$, with eigenvalue 1, and five initial translational energies and both initial rotational energies $J = 0$ and 1. Except for statistical variations (especially in the $T = 0.05$ eV distributions which was represented by only a small number of trajectories) the distributions for $J = 0$ and $J = 1$ were the same at each energy. Increasing the rotational quantum number by one had no discernible effect on these final state distributions.

1.B.2.c. Isotopic Substitution

Three isotopic variations of the molecular reagent were used with eigenvalue 1 (at five initial translational energies) and eigenvalue 2 (at three initial translational energies) and each with both $J = 0$ and $J = 1$. The product distributions from reaction with HD or D_2 exhibited the same general trends with respect to initial eigenvalue, initial translational energy and initial value of J as described in the previous sub-sections for reaction with H_2 . However, there were differences in the product distributions for the products arising from different isotopic reagents as depicted in figures 17 to 21. Four different relationships were possible for each distribution; (1) comparison of the OH and OD from reaction with H_2 and D_2 , (2) comparison of the OH and OD produced from reaction with HD, (3) comparison of the OH produced from reaction with H_2 and HD, and (4) comparison of the OD produced from reaction with D_2 and HD. To facilitate these comparisons, each variant was presented on the plots of the distributions, at each of four

Figure 14: Histogram plot of the reactive impact parameter distributions for the reaction $O^* + H_2$ and trajectories starting with eigenvalue 1 and $J=0$ or 1. The initial translational energy (T in eV) is given in each panel.

Figure 15: Histogram plot of the vibrational distributions for the reaction $O^* + H_2$ and trajectories starting with eigenvalue 1 and $J = 0$ or 1. The initial translational energy (T in eV) is given in each panel.

Figure 16: Histogram plot of the centre-of-mass scattering angle distributions for the reaction $\text{O}^* + \text{H}_2$ and trajectories starting with eigenvalue 1 and $J = 0$ or 1. The initial translational energy (T in eV) is given in each panel.

initial translational energies. In figures 17 to 21, the first column (labelled OH/H₂) is for the distributions of the OH product in the reaction with H₂, the second column (labelled OH/HD) is for the OH product in the reaction with HD, the third column (labelled OD/HD) is for the OD product in the reaction with HD, and the fourth column (labelled OD/D₂) is for the OD product in the reaction with D₂. For each figure the trajectories started with eigenvalue 1 and J = 0.

The impact parameter distributions are presented in figure 17. Except for statistical fluctuations, the distributions at each initial energy are the same for all four variations. The distributions for reagent D₂ had the same shape as those seen previously (and again here) for H₂ - a unit step function. This indicated that there was no steric factor in the reaction, that is, the more massive D-atoms were still sufficiently mobile to facilitate insertion for any initial approach.

The distributions for the number of times the trajectories entered the well are given in figure 18. Reaction with H₂ had a slightly greater percentage of direct reactions (0 or 1 times in the well) than the other variations. Direct reaction accounted for 29, 22, 26, and 27% of the OH/H₂, OH/HD, OD/HD, and OD/D₂ reactions respectively. The greatest difference was for the OH/HD which had noticeably fewer direct reactions than the other three variations. In the reaction with HD the ratio of 0 to 1 times in the well differed; the OH product was formed without entering the well more readily than the OD product despite having fewer direct reactions. The distributions for the OH product differed for production from H₂ or HD. Reaction with H₂ was accompanied by a greater percentage of direct reaction. The OD distributions were similar for both reagents (HD or D₂). As noted earlier for the H₂ reaction, all three isotopic variants had an increasing percentage of direct reactions as the initial translational energy increased. For

Figure 17: Histogram plot of the reactive impact parameter distributions for the four isotopic variations; OH from H₂, OH from HD, OD from HD, and OD from D₂. All trajectories started with eigenvalue 1 and $J = 0$. The initial translational energy (T in eV) is given in each panel.

Figure 18: Histogram plot of the number of times the average trajectory entered the H₂O well for the four isotopic variations; OH from H₂, OH from HD, OD from HD, and OD from D₂. All trajectories started with eigenvalue 1 and $J = 0$. The initial translational energy (T in eV) is given in each panel.

trajectories with initial kinetic energy of 0.5 eV, direct reactions had increased to 38, 35, 39, and 33% for the OH/H₂, OH/HD, OD/HD, and OD/D₂ respectively. Reaction with D₂ had the smallest increase in direct reactions with increasing energy.

The distributions of final vibrational level are given in figure 19. The OD distributions always extend to higher values of the vibrational level than the OH distributions, as expected, due to the smaller vibrational constant for OD. Taking into account this necessary difference, the distributions for the product from H₂ or D₂ were similar within statistical variations. The OH distributions from H₂ and HD were very similar at all energies. The OD product from HD was, however, radically different when compared to either the OH product from the same reaction or the OD product from reaction with D₂. It was highly inverted at all initial conditions, peaking in $v' = 2$. The OH/HD and OD/D₂ distributions were more excited than statistical but monotonically decreasing. In addition, the OD/HD had more of the reaction exoergicity partitioned into vibration than any of the other variations. The fraction partitioned into vibration for the four variations at an initial translational energy of 0.084 eV was $f_{v'}$ = 0.38, 0.40, 0.45, and 0.36 for OH/H₂, OH/HD, OD/HD, and OD/D₂ respectively. The only point of similarity between OD/HD and the other variations was that its distribution also became (more) inverted as the initial translational energy increased.

The rotational distributions are given in figure 20. Again, due to the smaller rotational constant, the distributions for OD extended to higher values of J than the OH counterparts. The OH/H₂, OH/HD and OD/D₂ distributions were individually similar in shape at each energy. The OD/HD distributions peaked at a lower J value than the OD/D₂, which was expected due to the larger amount of the reaction energy partitioned to vibration.

Figure 19: Histogram plot of the vibrational distributions for the four isotopic variations; OH from H₂, OH from HD, OD from HD, and OD from D₂. All trajectories started with eigenvalue $\bar{I}$ and $J = 0$. The initial translational energy (T in eV) is given in each panel.

Figure 20: Histogram plot of the rotational distributions for the four isotopic variations; OH from H₂, OH from HD, OD from HD, and OD from D₂. All trajectories started with eigenvalue Γ and $J = 0$. The initial translational energy (T in eV) is given in each panel.

Despite rather large statistical deviations, the distributions for molecular scattering angle (figure 21) were similar for all variations with increased forward-backward scattering as the translational energy increased commensurate with the increase in direct reactions.

Figure 21: Histogram plot of the centre-of-mass scattering angle distributions for the four isotopic variations; OH from H₂, OH from HD, OD from HD, and OD from D₂. All trajectories started with eigenvalue $\bar{l}$ and $J = 0$. The initial translational energy (T in eV) is given in each panel.

I.B.3 Final State Correlations

In sub-section I.B.2.a, trajectories were termed direct if they accessed the H_2O well zero or one times. In addition, it was indicated that these trajectories were responsible for the hotter than statistical distribution of vibrational excitation for trajectories starting on eigenvalue 1. This assignment of vibrational excitation to direct trajectories is borne out by double variable correlations. Figure 22 is a double variable histogram plot of the correlation between vibrational excitation and the number of times in the well at two initial translational energies. The distributions plotted in figure 22 are for the reaction $\text{O}^* + \text{H}_2$ with $J = 0$, initial translational energies of 0.084 eV (the five panels on the left) and 0.7 eV (the five panels on the right) and starting with eigenvalue 1. Trajectories that never entered the well (the bottom panel for each energy) populated almost exclusively vibrational levels 0 and 1, with the greatest population in $v' = 1$. Those that entered the well once (the second from the bottom panels) produced an inverted vibrational distribution peaking in $v' = 1$. Those that entered the well 2, 3, or 4 times (the three top panels) typically gave a monotonically decreasing vibrational distribution. The distribution for well = 4 at 0.7 eV peaked in $v' = 1$ due to the poor statistics resulting from the small number of trajectories contributing to this distribution. Thus, the direct trajectories produced inverted vibrational distributions while those that resulted in formation of a long-lived collision complex gave a more statistical distribution. Analysis of the trajectories gave no indication why zero times in the well populated almost exclusively $v' = 0$ and 1. If these trajectories reacted by an abstraction mechanism, greater vibrational excitation would be expected.

Double variable histograms for the rotational distributions corresponding to the number of times in the well (figure 23) indicated that direct reaction and long-lived collision

Figure 22: Double variable histogram plots of the vibrational distributions for 0 to 4 times in the well. All distributions are for the reaction $\text{O}^* + \text{H}_2$ starting with eigenvalue 1, $J = 0$, and initial translational energy of 0.084 or 0.7 eV. The value of times in the well (WELL) to which each distribution corresponds is given in each panel.

J' as a Function of Times in the Well

 $T=0.084\text{eV}$
 $T=0.7\text{eV}$

Figure 23: Double variable histogram plots of the rotational distributions for 0 to 4 times in the well. All distributions are for the reaction $\text{O}^+ + \text{H}_2$ starting with eigenvalue 1, $J=0$, and initial translational energy of 0.084 or 0.7 eV. The value of times in the well (WELL) to which each distribution corresponds is given in each panel.

Figure 24: Double variable histogram plots of the centre-of-mass scattering angle distributions for 0 to 4 times in the well. All distributions are for the reaction $\text{O}^+ + \text{H}_2$ starting with eigenvalue 1, $J = 0$, and initial translational energy of 0.084 or 0.7 eV. The value of times in the well (WELL) to which each distribution corresponds is given in each panel.

complexes produced the same distributions. The rotational distributions for times in the well from 0 to 4 were the same within the errors of the distributions and were consistent with the total distributions for the two energies (figure 23).

The correlation between scattering angle and number of times in the well is shown by the double variable histograms plotted in figure 24. For both energies the forward-backward scattering comes principally from trajectories entering the well 1 or 2 times. Those that entered the well once were predominantly scattered forwards and those that entered twice were scattered backwards. The trajectories that entered the well 3 or more times had a more flat distribution of scattering angles consistent with the expected statistical distribution from a long-lived collision complex. The number of trajectories with an initial translational energy of 0.084 eV that did not enter the well (Well = 0) was too small to give a statistically significant distribution. The distribution for 0 times in the well at 0.7 eV had forward-backward symmetry which could indicate that in the mechanism responsible for these trajectories either bond had an equal probability of breaking.

I.B.4. Dynamical Effects

In the reaction $O^* + H_2$ the initial azimuthal angle was limited to the first quadrant *i.e.* its range was from 0 to 90° instead of the normal range of 0 to 180° which is usually required in trajectory calculations. This restriction was valid since inclusion of the angles from 90 to 180° was redundant due to the symmetry of the H_2 molecule. As a result, additional insight into the dynamics of the reaction was gained since it could be determined which H-atom formed the OH product, the one closest to the O^* -atom as it approached or the one furthest from it. The separate contributions of these two channels to the various distributions for this reaction could be determined since the trajectory program listed them as separate products. These two channels are labelled 'near' and 'far' in the discussions below depending on whether the H-atom initially nearest to or furthest from the incident O^* -atom bonded to form the OH product. In the histogram plots for this sub-section the four panels on the left labelled $H_1 + OH_2$ are for the far channel at different initial translational energies and those on the right labelled $H_2 + OH_1$ are for the near channel.

The far channel was produced predominantly by trajectories that entered the H_2O well only once (figure 25) while the near channel had a substantially smaller contribution from trajectories that entered the well only once. This trend became more dominant as the collision energy increased. The vibrational excitation was consistent with the contributions of direct reactions to these separate channels (figure 26). The far channel, which had a greater contribution from direct reactions, was more excited vibrationally than the near channel. The vibrational distribution for the far channel was already inverted for an initial translational energy of 0.3 eV while that for the near channel remained monotonically decreasing for all energies.

Figure 25: Histogram plots of the number of times the average trajectory entered the H_2O well for far ($H_1 + OH_2$) or near ($H_2 + OH_1$) reactions. All distributions are for the reaction $O(^1D) + H_1H_2$ starting with eigenvalue 1 and $J = 0$. The initial translational energy (T in eV) is given in each panel.

Figure 26: Histogram plots of the vibrational distributions for far ($H_1 + OH_2$) or near ($H_2 + OH_1$) reactions. All distributions are for the reaction $O(^1D) + H_1H_2$ starting with eigenvalue 1 and $J = 0$. The initial translational energy (T in eV) is given in each panel.

The far channel had a greater contribution to scattering in the forward direction while the near channel had a greater contribution to backward scattering (figure 27). This was consistent with the results presented in sub-section I.B.3. Trajectories that entered the well once were predominantly forward scattered and those that entered twice were backward scattered. Since the far channel was produced predominantly in trajectories that entered the well once, it was forward scattered while the near channel which had a greater contribution from trajectories entering the well twice was backward scattered. Both channels also had an underlying flat distribution at all scattering angles resulting from the trajectories contributing to them that formed a long-lived collision complex.

Figure 27: Histogram plots of the centre-of-mass scattering angle distributions for far ($H_1 + OH_2$) or near ($H_2 + OH_1$) reactions. All distributions are for the reaction $O(^1D) + H_1H_2$ starting with eigenvalue 1 and $J=0$. The initial translational energy (T in eV) is given in each panel.

I.B.5. Branching Ratios

The branching ratio of greatest significance is the OD/OH ratio from the reaction $O^* + HD$ since this value can be measured experimentally. The values for this ratio can be determined from the number of type 2 (OD) and type 3 (OH) trajectories resulting from each set of initial conditions which are listed in table 1. The values listed in table 1 of the type 2/type 3 ratios correspond to the OD/OH ratios in the reaction $O^* + HD$. The OD/OH ratio *increases* with increasing initial translational energy from 1.54 at 0.03 eV to 2.18 at 0.5 eV for trajectories starting with eigenvalue 1. The ratios for $J = 1$ are slightly larger than those for $J = 0$ at the lower energies and *decrease* with increasing initial translational energy. For trajectories starting with eigenvalue 2, the OD/OH ratios are substantially larger than those for eigenvalue 1 and *decrease rapidly* with increasing energy for trajectories starting with $J = 0$. The OD/OH ratios for trajectories starting with eigenvalue 2 and $J = 1$ were notably smaller than those starting with $J = 0$ and *changed very little* as the initial translational energy increased.

The type 2/type 3 ratios in the reactions $O^* + H_2$ and D_2 are of dynamical interest. Type 2 trajectories indicate that the OH (OD) product was formed with the H (D)-atom originally furthest from the incident O^* -atom and type 3 from the H (D) originally nearest. For trajectories starting with eigenvalue 1 and $J = 0$, in both reactions (H_2 and D_2) the near product is slightly favored at low collision energies while the far product is more notably favored at higher collision energies. Trajectories starting with eigenvalue 1 and $J = 1$ had an almost constant ratio of around 1 at all initial translational energies.

Trajectories that started with eigenvalue 2 and $J = 0$ strongly favored the near product as would be expected from reaction by collinear abstraction. As the collision energy increased, however, the percentage of far products increased rapidly to around 25% of

the reactive collisions at 0.7 eV (as opposed to only 5% or less at 0.3 eV). This increase in far reactions cannot be accounted for entirely by the increase in the number of trajectories that returned to form an insertion intermediate after changing surfaces in the exit channel (15% entered the H₂O well 1 or more times at 0.3 eV and 26% at 0.7 eV for the reaction O* + H₂). In the reaction O* + D₂, those trajectories with J = 1 that started with eigenvalue 2 had a constant ratio for all energies with far reactions comprising approximately one third of all reactive collisions. The eigenvalue 2, J = 1 trajectories for the reaction O* + H₂ reacted predominantly with the *far* H-atom at low energies and with the *near* H-atom at higher initial translational energy.

I.C. Discussion: Trajectory Calculations

In the previous sections, a rather large amount of information has been presented, although it represents only a small fraction of the total data obtained in this study. From the various distributions for each parameter at the different initial conditions, several conclusions can be made. Since previous trajectory studies have been limited to only the lowest eigenvalue, the distributions for this eigenvalue will be discussed first.

In this study, there were two aspects that dominated the trajectories: the mobility of the H_2 molecule and the influence of direct (entering the H_2O well 0 or 1 times), as opposed to long-lived, collisions. The mobility of the H_2 molecule and the fact that the lowest potential surface decreased monotonically from any configuration to the H_2O minimum enabled the H_2 to re-orient itself to an insertion geometry from almost any initial orientation. This was clearly displayed in the trajectory depicted in figure 7 where the O^* -atom initially approached the H_2 molecule nearly 'end-on' and yet underwent insertion. This mobility of the H_2 molecule is also reflected in the distribution of the reactive impact parameters. The opacity function for these reactions was very close to a unit step function. This indicated a lack of steric hindrance to these reactions. The effect of this mobility extended to the HD and D_2 reactions as well, as evidenced by the unit step function shape of their opacity functions. Even at higher initial translational energies (thus a more rapid approach of the O^* -atom to the H_2 molecule) this re-orientation is still possible. The only effect on the impact parameter of increasing the initial translational energy was to decrease the maximum reactive impact parameter, consistent with an R^{-6} long range potential (expected for reaction of an atom with a diatomic) without a barrier.

The vibrational and scattering angle distributions showed the greatest influence of direct trajectories. The percentage of direct trajectories contributing to reaction at each set of initial conditions is obtained from the distributions of the number of times in the well. The percentage of direct trajectories increases with increasing initial translational energy from 29% at 0.084 eV to 46% at 0.7 eV. Increasing the initial rotational energy to $J = 1$ has no obvious effect on the percentage of direct trajectories. Those trajectories entering the well 2 or more times are well described by unimolecular dissociation of a long-lived complex, as seen from the analysis of figure 10. Those trajectories entering the well 0 or 1 times have inverted vibrational distributions giving total vibrational distributions that are, at low initial translational energies, monotonically decreasing but 'hotter' than statistically expected. At high initial translational energy, the total vibrational distribution becomes inverted, reflecting the increase in direct reactions. The vibrational distributions for OH from H_2 and HD, and for OD from D_2 are similar at analogous energies, again reflecting the percentage of direct reactions. The OD from HD is inverted at all initial translational energies even though it has a similar percentage of direct reactions as the other isotopic variations. The dynamical reason for this is unknown. The vibrational distributions obtained in this study compare very well with those of Fitzcharles and Schatz³ even to the inversion for OD from HD. The only other deviation in the vibrational distributions is for the far reactions which became inverted at a lower initial translational energy than what the total vibrational distribution did, while the near reactions did not invert at any energy used in this study. This is explained by the percentage of direct trajectories since the far reactions are produced almost exclusively by trajectories that entered the well once and the near trajectories had a much larger contribution from long-lived collision complexes.

The distribution of scattering angles is forward-backward peaked overlying an essentially flat distribution at all angles. The distribution becomes more peaked in the forward-backward directions with increasing initial translational energy and is unaffected by increasing the rotational energy to $J = 1$. From figure 24, these two features are seen to be due to direct and long-lived trajectories: entering the well 0 times produces forward-backward peaks, entering once is predominantly forward, twice is backward and 3 or more times has increasing contributions at all angles. The other isotopic variations also have forward-backward peaking which becomes more predominant with increasing initial translational energy. The distributions for the near and far trajectories are more peaked in the backwards and forwards directions respectively. The dynamical reason for this has not been determined in this study, although it appears to be related to the fact that far trajectories are produced predominantly with only one excursion into the well while near trajectories have a greater contribution from 2 excursions into the well.

The rotational distributions are less notably affected by either of these effects, the mobility of the H_2 molecule and the percentage of direct trajectories. At low initial translational energy, the distribution is substantially 'hotter' than statistically expected, although this is not due to direct reactions as indicated in figure 23: the rotational distributions for times in the well from 0 to 4 are all 'hotter' than statistical. This non-statistical distribution is expected to be the result of angular momentum constraints rather than the dynamics of the reaction. In a *statistical* simulation of the RRKM unimolecular decomposition of the energetic H_2O intermediate formed by insertion in this reaction, Holmlid and coworkers²⁰⁻²² obtained a *non-statistical* 'hot' rotational distribution due to angular momentum constraints. This angular momentum constraint could also dominate the distribution from direct reactions. As the initial translational energy increases the rotational distribution peaks at lower values of J' and becomes more symmetrically

distributed about the peak. Since there is a larger percentage of direct trajectories as the initial translational energy increases, the distribution would not be expected to become more statistical as might be expected if the percentage of long-lived trajectories increased. The fraction of the reaction exoergicity channeled into vibration remained constant at all energies, therefore there is no apparent reason for this change in the rotational distribution. There is no discernible effect on the rotational distributions due to increasing the initial rotational energy to $J = 1$. Isotopic substitution also has little effect on the rotational distributions with the exception that the OD from HD is slightly colder than the other variations at analogous energies due to the increased fraction of the reaction exoergicity channeled into vibration for this variation ($f_{v'} = 0.45$ as opposed to 0.38, 0.40, and 0.36 for OH/H₂, OH/HD, and OD/D₂ respectively). In the trajectory calculations of Fitzcharles and Schatz³ the OD product from D₂ was similarly found to be rotationally colder than the other isotopic variations.

This DIM study is the first to explore the effects of reaction on the second eigenvalue surface and therefore cannot be compared to previous results. Eigenvalue 2 trajectories are of increasing importance for reaction at hyperthermal energies. They have markedly different distributions from those which start with eigenvalue 1. These differences are primarily due to the different reaction mechanism (abstraction) for these trajectories. The abstraction mechanism for reaction on this second eigenvalue surface is substantiated by several of the distributions. At low (0.3 eV) initial translational energy the distribution of impact parameters is peaked at $b = 0$ and is monotonically decreasing to a maximum reactive impact parameter value that is much smaller than that for trajectories starting with eigenvalue 1 at the same energy. There is very high vibrational excitation, with the vibrational distribution inverted (peaking in $v' = 4$) and a large fraction of the reaction exoergicity channeled into vibration ($f_{v'} = 0.49$). Only a small percentage (15%) of the

reactive trajectories entered the H_2O well. The scattering angle was peaked in the backwards direction. A plot of a typical eigenvalue 2 trajectory (figure 6 (a)) shows that only one O-H distance attains reasonably small values while the other O-H distance is always substantially larger. Finally, 95% of these trajectories reacted with the near H atom. All of these together provide a convincing argument that eigenvalue 2 trajectories react by near-collinear abstraction. The only distribution that is not consistent with an abstraction mechanism is the rotational distribution. It is much 'hotter' than would be expected for this mechanism. This, however, is due to angular momentum constraints which have already been encountered for trajectories starting with eigenvalue 1 and should be operative for these trajectories as well.

There are, however, certain characteristics of the eigenvalue 2 trajectories at higher initial translational energy (0.7 eV) that cannot be adequately explained by an abstraction mechanism or the increased contribution of insertions (the percentage of trajectories that entered the well increased from 15% at 0.3 eV to 26% at 0.7 eV). The distribution of impact parameters peaks at 1.5 bohrs, the vibrational distribution is less inverted with a decreased fraction of the reaction exoergicity partitioned into vibration ($f_{\text{vib}} = 0.41$), there appears to be a second low- J' ($J' = 5$) peak in the rotational distribution, the distribution of scattering angles is predominantly flat with a slight *forward* peak, and the percentage of far trajectories increases by 20% over that found at 0.3 eV. A collinear abstraction mechanism is completely incapable of producing the observed changes in the vibrational distribution, the forward peaking in the scattering angle, and the increase in the percentage of far trajectories. At this higher initial translational energy the cone of acceptance (the cone of initial approaches that can lead to reaction, *i.e.* approaches that are more non-collinear) would increase and could shift the peak of the impact parameter distribution but it would also be expected to produce greater rotational excitation rather

than a low- J' peak. In addition, these non-collinear trajectories would not necessarily contribute to the increased percentage of trajectories that accessed the H_2O well since the Σ - Π intersection (which the trajectory must pass through before it can propagate on the lower eigenvalue surface) occurs in the *exit* channel only and the initial configuration may have no effect on whether the trajectory returns to insert or continues to propagate along the exit channel. This correlation has not been investigated in this study. These non-collinear trajectories would, as well, not be able to produce the increase in far reactions and the forward peaking of the scattering angle. The increased percentage of inserting trajectories (from whatever source) cannot be responsible for the changes in the distributions since they increased by only 11%, would contribute to higher rotational states rather than lower, could not incur a 20% increase in far reactions, and would contribute to all scattering angles not a forward peak. Another reasonably simple mechanism which could explain many of the distribution changes is 'stripping', where the incident O^* -atom passes the nearer H-atom without interaction and passes on to the further H-atom with which it does react. It is difficult to envision how this type of mechanism could be operative since the O^* -atom must avoid a 'close' encounter with the H_2 molecule as it approaches C_{2v} geometry on the *second* eigenvalue surface and would thus be too far from the second H-atom to interact. It is possible that these three types of trajectories (non-collinear, inserting, and stripping) combined produce the observed changes in the 0.7 eV eigenvalue 2 distributions but this would be very difficult to confirm.

The OD/OH branching ratio is notably different for trajectories starting on eigenvalue 2. It is substantially larger than the eigenvalue 1 ratio. At 0.3 eV the eigenvalue 2, OD/OH ratio is 7.26. It must be stressed that for the HD reaction the full azimuthal range of 0 to 180° was used and therefore equal numbers of trajectories at each set of initial conditions

were initially directed towards the H-atom end of the HD molecule as towards the D-atom end. The dynamical reason why OD production is strongly favored over OH production in an abstraction mechanism has not been determined in this study. In addition, the eigenvalue 2 OD/OH branching ratios decreased with increasing initial translational energy for initial rotational energy of $J = 0$ whereas the $J = 1$ ratios remained almost constant at a value between 3 and 4 for all initial translational energies. A similar tendency also occurred for the near/far ratios for initial rotational energy of $J = 1$ and the D_2 reactions. In these trajectories the near/far ratios for all initial translational energies lay between 0.55 and 0.6. Again, the dynamical reason for this difference has not been determined in this study. The type 2/type 3 ratios for trajectories starting with eigenvalue 2 and $J = 1$ for the H_2 reaction are notably different from those for the HD and D_2 reactions. At low initial translational energy these trajectories favor far reaction and at high energy they favor near reaction. The dynamical reason for this has not been investigated in this study, but is expected to be due to a correlation between the time of approach of the O^* -atom prior to strong interaction and the time required for the H_2 molecule to execute half of a rotation.

The final comparisons must be made against experimentally determined values for these reactions. These are the vibrational and rotational distributions for the OH (OD) product, the distribution of molecular scattering angles, and the OD/OH ratio from reaction with HD. This comparison is complicated since contributions for reaction on the two lower eigenvalue surfaces should be included. However, the experimental results were all obtained at collision energies below the barrier on the $^1\Pi$ surface and would have very small contributions (resulting from the high energy tail of a thermal Maxwell-Boltzmann distribution) from reaction on the second eigenvalue surface. In addition, the eigenvalue 2 trajectories are characterized by very small reactivities (comprising only 7% of the total

reactivity at 0.3 eV). As a result, the experimental values will be compared to the eigenvalue 1 results only.

The vibrational distribution from the reaction $O^* + H_2$ has been measured by several investigators by various methods⁷⁻¹². The most recent results are listed in table 3 along with the distribution obtained in this study at 0.084 eV: the initial translational energy closest to the reaction energy expected when photolysis of ozone in the Hartley band is the source of O^* . From the values listed in table 3, the distribution obtained in this study does not display the marginal inversion found by Aker and Sloan⁹ or the rapid drop-off between levels 2 and 3 found by Cleveland *et al.*¹¹. The monotonically decreasing vibrational distribution of Huang *et al.*¹² most closely matches this trajectory distribution. The experimentally determined vibrational distributions obtained by different investigators (by three different techniques) do not have good agreement even within themselves, although they all indicate greater than statistical vibrational excitation. It is, therefore, difficult to determine whether the vibrational distribution obtained in this trajectory study agrees adequately with the 'correct' distribution. A two dimensional quantum trajectory calculation²³ showed higher vibrational excitation than its classical counterpart. This indicates that quantum effects may have a strong influence on this reaction. The quantum calculation gave an inverted vibrational distribution, similar to that found experimentally^{9,10}. This indicates that the vibrational distributions obtained in the trajectory calculation presented here are not sufficiently excited.

The distributions for the isotopic variations are also listed in table 3. Again, the results are not in very close agreement with experiment, lacking the inversion found by Butler *et al.*¹⁰ for OH/HD and OD/D₂, and being too inverted for the OD/HD.

Table 3: Comparison of the product vibrational distributions obtained in this trajectory study to the most recently determined experimental distributions. Normalization is such that the vibrational level with the greatest population in each distribution is equal to 1.0.

Reaction	$v' = 0$	1	2	3	4	5	6	Reference
OH/H ₂	1.0	0.897	0.557	0.321	0.125	0.005		this work
	-	0.91	1.0	0.78	0.41			9
	0.96	1.0						10
	-	-	1.0	0.34				11
	1.0	0.69	0.63	0.51	<0.36			12
OH/HD	1.0	0.719	0.530	0.417	0.170	0.003		this work
	0.98	1.0						10
OD/HD	0.854	0.991	1.0	0.864	0.673	0.455	0.163	this work
	0.75	1.0	0.86					10
OD/D ₂	1.0	0.880	0.628	0.473	0.320	0.163	0.050	this work
	0.83	1.0	0.58					10

Experimental rotational distributions have also been determined^{6,10,11}. The experimental distributions are more excited than statistical with peaks at $J' = 26, 18,$ and 13 for OH vibrational levels 0 (reference 6), 2 and 3 (reference 11) respectively. The peaks in the rotational distributions obtained in this study, at an initial translational energy of 0.084 eV, are $25, 18,$ and 14 for the comparable vibrational levels. The agreement between this trajectory study and experiment is very good. In addition, Butler *et al.*¹⁰ found that the rotational distribution for OD/HD was slightly colder than that for OD/D₂, a result obtained in this trajectory study, which has been discussed above.

The centre-of-mass scattering angle has been measured by Buss *et al.*²⁴ for the reaction $O^* + H_2$ at a mean collision energy of 0.12 eV. They found symmetrical forward-backward peaks overlying a reasonably flat background that was approximately one third of the height of the peaks. The scattering angle distribution obtained in this trajectory study at an initial translational energy of 0.084 eV agrees very well with this experimental result. The distribution obtained in this study is forward-backward peaked overlying a flat distribution and between the angles of 40° to 140° has an average value of 0.37 . Since the scattering angle distributions obtained in this study become more peaked as the initial translational energy increases, a trajectory calculation at the slightly higher energy used in the experiment would give very good agreement.

The OD/OH branching ratio has been measured by Tsukiyama *et al.*²⁵ to be 1.13 . The OD/OH branching ratio (1.68) obtained in this study at an initial translational energy of 0.084 eV does not agree within the error bars with this experimental result.

I.D. Conclusions: Trajectory Calculations

The high mobility of the H_2 molecule and the shape of the lower eigenvalue potential surface makes insertion the predominant mechanism for trajectories that start with eigenvalue 1. In addition, those trajectories that undergo a direct reaction give product distributions that agree well with experimentally determined distributions. It is predominantly the contribution from trajectories that form long-lived collision complexes that distort the total distributions from the desired ones.

Trajectories that start on the second eigenvalue surface react by abstraction and have notably different product distributions from those for trajectories that start on the lower eigenvalue surface. In addition, there are several features of the eigenvalue 2 product distributions at higher initial translational energy that cannot be readily explained.

The surfaces used in this trajectory study appear to be a reasonable empirical potential surface for the reaction $O^* + H_2$. In addition, the inclusion of the second eigenvalue surface appears to be essential for the proper modeling of this reaction, not only due to the influence that the intersections have on trajectories but also due to the dramatically different distributions that it produces. Recent *ab initio* calculations on the entrance channels for this reaction²⁶ has a collinear abstraction barrier on the $^1\Pi$ surface of only 0.105 eV. This barrier is now within the range of the mean reaction energies typically employed in the experimental studies of this reaction and increases the importance of this surface to trajectory results.

The original intent of this trajectory study - to model the reaction of O^* with halogenated methanes - does not appear to be successful since the HD and D_2 molecules are still sufficiently mobile to make insertion the predominant reaction mechanism for trajectories

starting on the lower eigenvalue surface and replacing one of the H-atoms in H_2 by a D-atom does not adequately represent the more massive C-atom in the halogenated methanes.

II. $O(^1D_g)$ + Halogenated Methane Reactions

II.A. General Description: Experimental

II.A.1 Introduction: Experimental

Ozone is a major constituent of the stratosphere and its strong absorption of solar radiation in the middle ultraviolet (the Hartley band, peaking around 250 nm) is essential for the survival of the biological organisms inhabiting the troposphere. With normal atmospheric composition, the production and consumption of ozone forms a closed cycle, with $O(^1D)$ atoms playing a minor role. The principal reactions are:

The only contribution $O(^1D)$ makes to this system of reactions is as a source of $O(^3P)$ atoms as a result of collisional quenching by the major constituents of the lower stratosphere O_2 and N_2 ; $O(^1D)$ is metastable with a radiative lifetime²⁷ to the ground state (at 630 nm) of 140 s and reaction with the major stratospheric constituents is much slower than quenching. However, trace amounts of atmospheric pollutants (particularly N_2O , hydrocarbons and freons) provide an alternate channel for $O(^1D)$ removal - by reaction. The reaction rate of $O(^1D)$ with many common pollutants is very fast, typically on the order of the gas kinetic collision rate (around $10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$). These

reactions decrease the overall production of $O(^3P)$ and alter the balance between $O/O_2/O_3$ in the lower stratosphere. Of greater significance, some of the products of these reactions are then involved in the catalytic, ozone destroying cycles:

where $X = OH, NO, F, Cl,$ or Br . These catalytic cycles have the capacity to seriously alter the ozone concentration even though the atmospheric contaminants from which they originate are in trace amounts. As a result, study of the reaction of $O(^1D)$ with pollutants that have these catalytic agents as products is essential for accurate stratospheric modeling. Halogenated methanes are not only included amongst the pollutants that require study, but they are reasonably simple and an understanding of the dynamics of these reactions would provide insight into reactions with more complex freons.

There is, as well, a more esoteric reason for studying these reactions; to understand the dynamics involved in polyatomic reactions. As a result of the electronic excitation of the $O(^1D)$ atom, it has been experimentally determined that it is highly reactive, with large exothermicities, little or no barrier to reaction, and its insertion into $X-H$ bonds forms an intermediate that is a stable molecule. These characteristics make it an ideal choice for both experimental and theoretical study.

Trajectory calculations for atom-polyatomic reactions are now tractable and feasible with the high-speed computers that are becoming readily available. In addition, potential surfaces for various methanols have already begun to appear^{28,29}. Halogenated methanes should have potential surfaces that are quite similar to that of methane; the halogen atom

requires one electron to form a closed shell similar to hydrogen and should have a similar type of bonding as the hydrogen atom that it replaces in these molecules. Slight variations in the dynamics for the different substitutions will provide sensitive tests for eventual trajectory calculations for these molecules.

Throughout this section, most of the reactions will be discussed in term of the mechanism by which the product is formed. In order to avoid ambiguity, the terms used for these mechanisms are defined below, using the reaction $\text{O}(^1\text{D}) + \text{CH}_4$ as a prototype. These are not general definitions of the terms but rather their specific meaning as used in subsequent sections.

For this thesis, two reaction mechanism categories (abstraction and insertion) are considered with sub-mechanisms belonging to each. *Abstraction* is chemically the simplest of the two since it involves only the formation of one new bond and the prompt breaking of one old bond. In this mechanism, the O-atom approaches one of the H-atoms in a direction that is nominally collinear to the existing C-H bond and forms a bond with the H-atom.. The approach need not be collinear or even close to it provided that the O-atom does not come near enough to the other atoms in the molecule (one C-atom and three H-atom in the prototype reaction) to sufficiently interact with them for an additional 'bond' to form (the cases when these do occur represent other mechanisms and are discussed below). The O-atom forms a bond exclusively with the H-atom it is approaching, and as it 'rebounds' after the collision, this new bond persists and the old bond between the H-atom and the C-atom breaks. The expression 'rebound' is used to indicate the relative motion of the products in the *centre-of-mass* frame and gives no indication of the product motions in the *laboratory* frame. This type of mechanism is characterized by backward scattering in the centre-of-mass frame and low to moderate

rotational excitation depending on whether the collision was collinear to the bond existing in the reactant or not, respectively. The vibrational and translational excitations depend on the mass combinations and the nature of the potential surface. A representative correlation diagram for the reaction $\text{O}(^1\text{D}) + \text{HR}$ is given in figure 28. The energy levels on the right side of the diagram represent the energetics as the reaction passes through the point of closest approach for a collinear abstraction and then separates into products. Note that this diagram exhibits correlations and the locations of the energy levels are indicative only. The relative spacing of the levels will vary according to the individual reaction considered although those depicted here are typical. From this diagram, it is seen that abstraction occurs on a monotonically decreasing potential surface and does not form a stable intermediate at any point. The reaction is direct and does not form a long-lived complex, that is, the lifetime of the complex is less than a couple of rotations. As a result, it cannot be collisionally stabilized and must either return to the reactant channel or form $\text{OH} + \text{R}^\cdot$ products.

The second mechanism that is relevant to the reactions discussed below is *insertion*. During insertion, the O-atom forms a bond with both an H-atom and the C-atom in the prototype reaction (one case of the 'double' bonds disallowed in the abstraction mechanism). The O-atom approaches the molecule approximately perpendicular to the C-H bond that it is interacting with. The C-H bond under attack breaks and the O-atom bonds with both the C-atom and the H-atom thus released. The approach does not have to be strictly perpendicular to the old bond, as long as the O-atom gets sufficiently close to the C-atom for the new bonds to form. There are several subsequent processes after insertion that result in different products. Some of the product channels can be attained by different mechanistic processes and the term used to indicate how the product has been generated differentiates between them. *Atomic substitution* indicates that the

Figure 28: Typical energetics of the insertion (left) and abstraction (right) intermediates for the reaction $O^* + RH$ leading to formation of OH (using $O^* + CH_4$ as a prototype). Energies are in kJ/mole.

H-atom which formed the new bond with the incident O-atom is promptly released, breaking one of the newly formed bonds and the products are the H-atom and a methoxy radical. *Molecular elimination* occurs when the newly formed O-H bond promptly breaks and the H-atom thus released subsequently interacts with one of the other H-atoms in the molecule and bonds with it which causes the dissolution of the C-H bond of this second H-atom. In this case the products are H_2 and a carbonyl (formaldehyde). This two step process would be expected to produce 'hot', non-statistical rotational and vibrational distributions. The other mechanism with a short-lived collision complex is *insertion-elimination*. In this case, the O-atom inserts into the C-H bond and the new C-O bond breaks leaving OH and a methyl radical as the products. In section I of this thesis, it was seen that for the reaction $O^* + H_2$, insertion was the dominant mechanism and for those trajectories that resulted from a short-lived complex (assumed to be those that entered the H_2O well zero or one times) the OH vibrational distribution was inverted and there was substantial rotational excitation. Similar vibrational and rotational excitation would result following insertion-elimination from the methanes due to excitation of an antisymmetric stretch when the original C-H bond length increased to accommodate the incoming O-atom. The short lifetime of the complex would hinder redistribution of this excitation to the remainder of the complex before separation into products. The reaction exoergicity would appear as vibrational and rotational excitation in the OH product as well as translational excitation.

There are also several mechanisms resulting from a long-lived collision complex. On the left-hand side of figure 28 is depicted the typical energetics of an $O(^1D) + HR$ insertion. The collision complex formed by insertion corresponds to a highly excited, strongly bound, stable molecule. This collision complex can be stabilized if the lifetime of the complex is comparable to or longer than the collision time or the radiative lifetime of the

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populated state. If the collision complex undergoes either of these processes, a stable methanol product is formed. For the reactions considered in this thesis, the radiative lifetime of the excited methanol is on the order of 100 msec, which is much longer than the expected unimolecular dissociation lifetime of these excited methanols. As a result, this method of stabilization is not expected to have a significant contribution. These two mechanisms are considered indistinguishable and both will be termed *addition*. A long-lived, semi-stable molecule can also be formed if the lifetime of the complex is longer than that for intramolecular relaxation. However, unless the highly energetic methanol thus formed is collisionally stabilized (becoming an addition product), it will undergo *unimolecular decomposition* and the various channels open to it will be statistically populated.

There are two other processes by which products are formed that must be discussed, although they are closely related to two of those mentioned above. *Fragmentation* is a non-statistical form of unimolecular decomposition which can occur after insertion. In this process, the collision complex splits while the reaction exoergicity is still primarily retained in the vicinity of the bond at which insertion occurred. In this way, the fragment containing the O-atom can possess a large fraction of the reaction energy while the other fragment has a low-energy statistical distribution of internal states since the reaction exoergicity had not yet migrated to this portion of the collision complex prior to fragmentation. This process is not observed in the prototype reaction, but it could be represented by the formation of CH_2 and H_2O , with the latter product containing most of the exothermicity.

Predissociation, the final mechanism, can occur subsequent to many of the processes already discussed provided two conditions are met. These conditions are that the reaction

takes place on a potential surface that correlates with an electronically excited state of one of the molecular products and that this excited state is predissociative (for a comprehensive discussion of predissociation, see Herzberg^{30,31}). Both of these criteria are satisfied by the product channel $\text{H}_2 + \text{CH}_2\text{O}$ of the prototype reaction. The electronically excited state $\text{A}^1\text{A}''$ of CH_2O is energetically accessible to the reaction and correlates with the reactants and products when H_2 is formed in its ground state. It also predissociates into three different channels³² depending on the energy content of CH_2O^* . The lowest energy channel for this predissociation is to form H_2 and CO , resulting in the overall production of two H_2 molecules and CO from the prototype reaction. These same products are possible from unimolecular decomposition and these are distinct channels only by virtue of the formation time of the products and the distribution of the reaction exoergicity amongst the products. The initial production of H_2 and CH_2O are a result of one of the direct mechanisms and the lifetime of the collision complex and the energy partitioning into the products are consistent with the mechanism by which they are produced. The subsequent predissociation of the electronically excited molecular product is governed by its own dynamics, with its own characteristic lifetime and energy distribution. The same product channel resulting from unimolecular decomposition will have a statistical energy distribution and lifetime.

The reactions of $\text{O}(^3\text{P})$ with the molecules of interest to this thesis are several orders of magnitude slower^{33,34} than the analogous reactions with $\text{O}(^1\text{D})$, and proceed by substantially different dynamics: for reaction at an H-R or an H-X bond, $\text{O}(^3\text{P})$ does not correlate with the strongly bound intermediate resulting from insertion into the bond (whereas $\text{O}(^1\text{D})$ does), and abstraction of the H-atom dominates the reaction. The dynamics of $\text{O}(^3\text{P})$ reactions are reasonably well understood and there are several reviews³⁵⁻³⁷ which can be consulted. The reaction of $\text{O}(^3\text{P})$ with hydrides (HR where

R = H, Cl, OH, alkyl, etc.) proceeds by direct abstraction of the H-atom to form OH. The product OH is vibrationally hotter than is expected if the reaction energy were statistically distributed amongst all the energetically accessible internal and translational levels, which would occur if the reaction formed a long-lived intermediate. In addition, the OH rotational distribution in these reactions is typically peaked in the lower rotational states and decreases rapidly with J' -level with only a small fraction of the reaction energy partitioned into rotation. This is indicative of a collinear abstraction mechanism where the necessarily small impact parameter induces very little angular momentum (and thus rotation) into the collision. In the case where the radical is an unsaturated hydrocarbon, the preferred reaction is by addition to the unsaturated bond with subsequent decomposition to a number of products; the decomposition is complex and pressure dependent, and the reader is referred to the above mentioned reviews for more detail.

The literature pertaining to the reaction of $O(^1D)$ has increased very little in the past decade, except for its reaction with H_2 , which was discussed in the first section of this thesis, and CH_4 , which will be discussed, in part, below. The only general reviews of $O(^1D)$ reaction dynamics were given by Lin³⁶ and Whitehead³⁸ while Tully³⁹ and Wiesenfeld⁴⁰ have presented reviews specifically for reaction with atmospherically abundant molecules. A full survey of all of the studied reactions of $O(^1D)$ is beyond the scope of this thesis and only those concerned with n-alkanes and, where appropriate, alkanes will be discussed below. The analogous reactions with $O(^3P)$ will not be presented for each reaction discussed since they typically involve different potential surfaces. Reactions involving singlet methylene, $CH_2(a^1A_1)$ ⁴¹⁻⁴⁶, will be mentioned where appropriate since it is isoelectronic with $O(^1D)$ and should have similar potential surfaces and thus similar reaction mechanisms.

In the reactions of $O(^1D)$ with haloalkanes, there are three reaction sites that must be considered; at C-X bonds, at C-H bonds, and at C-C bonds (for those that have C-C and/or C-H bonds). Reaction at each of these sites will be discussed in turn for each class of reactions.

The reaction site that is easiest to discuss is the C-C bond. This bond is unreactive in the reaction of $O(^1D)$ with saturated hydrocarbons⁴⁷⁻⁵². These photochemical studies of the smaller polycarbon alkanes determined that cleavage of the C-C bond resulted only from decomposition of the excited alcohol (produced by insertion into a C-H bond and subsequent randomization of the energy to the remainder of the intermediate or collisional stabilization) and not from direct interaction at this bond. Halogen substitution would not be expected to alter the non-reactivity at this site. This expectation is supported by the reaction of singlet methylene with chloroalkanes⁴⁶ - reaction is restricted to C-H and C-Cl bonds with no evidence of direct interaction at the C-C bonds.

Various studies have probed the reaction at C-H bonds. Of the three possible interaction sites, this is the best studied, although the dynamics are still not fully elucidated. The earliest investigation in the gas phase⁵³ of the reaction of $O(^1D)$ with CH_4 established that the major reactive channel produced OH and CH_3 with substantial vibrational excitation of the OH, which led to the supposition that abstraction was the major dynamical mechanism. In a later study of this same reaction, in which the reactants were dissolved in liquid argon⁵⁴, the major product was found to be methanol (CH_3OH) which was construed to indicate that the major path was insertion, with minor paths being abstraction to form OH and molecular elimination of H_2 . To reconcile these two contradictory results, DeMore⁵⁵ suggested that the OH reaction channel passed through

the CH_3OH^* intermediate and did not occur by an (non-inserting) abstraction mechanism. This supposition was corroborated by the work of Cvetanovic and coworkers⁴⁷⁻⁵² on higher alkanes (propane, isobutane, neopentane, and cyclopentane); in each reaction the formation of OH was a major channel and the insertion intermediate could be stabilized collisionally to form the associated alcohol with a resulting decrease in OH production. This indicates that insertion was the dominant mechanism leading to elimination of OH if the insertion intermediate was not stabilized. From the total pressure required to stabilize the excited alcohol, Cvetanovic and coworkers estimated the lifetimes of the collision complexes to range from about 10^{-11} seconds for the propyl alcohol intermediate to 4×10^{-9} seconds for the neopentyl alcohol intermediate. These results indicated that the lifetime of the excited intermediate decreased dramatically as the number of carbon atoms in the alkane decreased. This trend was found to persist to the mono-carbon intermediate, methyl alcohol, for which Lin and DeMore⁵⁶ estimated a lifetime of about 8×10^{-13} seconds, and determined that it could not be significantly stabilized by collisions at pressures up to a hundred atmospheres. They determined that formation of OH constituted 80% of the reaction with half resulting from the insertion intermediate and half resulting from direct abstraction. Cvetanovic and coworkers also found this duality of mechanism associated with a single reaction channel for the reactions involving the higher alkanes⁴⁷⁻⁵². Paraskevopoulos and Cvetanovic determined that in the neopentane reaction⁵⁰ up to 66% of the reaction occurred by insertion (from the amount of neopentyl alcohol produced at high pressures) and only 25% from abstraction.

The study by Luntz⁵⁷ confirmed that two mechanisms are responsible for the OH reaction channel in the reaction of $\text{O}(^1\text{D})$ with alkanes. Luntz used laser induced fluorescence to determine the vibrational and rotational distributions of the OH resulting

from the reaction of $O(^1D)$ with saturated alkanes in the gas phase. The reaction was laser initiated by photolysis of O_3 , and the pressure and detection delay were adjusted to (presumably) avoid relaxation of the original distributions. The rotational distributions were found to be bimodal, *i.e.* with a rapidly decreasing peak in the lower levels and a broad distribution peaking in the higher rotational levels. These two rotational components were attributed to the abstraction and insertion components respectively; due to the impact parameters expected to contribute to these two mechanisms, the collisional angular momentum available to the products is expected to be very small for (collinear) abstraction and large for insertion. The high rotation (insertion) component produced a linear suprisal which facilitated the separation of the two components and extraction of their separate contributions to the vibrational distribution. From this analysis, Luntz determined that, for the abstraction component, the vibrational excitation decreased sharply with increasing numbers of carbon atoms: the ratio of the population of the second to the first vibrational levels ($P(v=1)/P(v=0)$) went from 1.0 for methane to ≤ 0.05 for neopentane. The rotational distribution for this component was sharply peaked in the lower rotational levels, was very similar for all four alkanes studied, was colder than statistically expected, and resembled the distribution found in the reaction of $O(^3P)$ with these alkanes. This latter observation suggested the possibility that the reaction proceeded by a singlet (the potential curves correlating with $O(^1D)$) to triplet (the potential curves correlating with $O(^3P)$) crossing, resulting in the $O(^3P)$ plus alkane abstraction dynamics dictating the product's rotational distributions; the rapidly decreasing vibrational excitation was due to the rapid dissipation of the reaction exothermicity to the remainder of the collision complex as the density of states increases with the number of carbon atoms. From the correlation diagram for this class of reactions, figure 28, it is seen that a singlet-triplet crossing does occur in the entrance

channel of the insertion surfaces. Theoretical⁵⁸ and experimental⁴⁷⁻⁵⁷ evidence indicates that the reaction of $O(^1D)$ with R-H bonds is typically by insertion and therefore along these surfaces in the entrance channel. In the analogous reaction of $O(^1D)$ with H_2 , the collision complex is not heavy enough to enhance the spin-orbit interaction and the total spin of a state is a constant of the motion, resulting in essentially no mixing of the two spin states. As a result, the singlet-triplet crossing does not contribute to the reaction with H_2 . Similarly, in the reaction of $O(^1D)$ with CH_4 , quenching of $O(^1D)$ to $O(^3P)$ (via the singlet-triplet crossing) is zero⁵⁹ while that for higher alkanes is very small⁴⁹. The large branching ratio into the abstraction component for the higher alkanes is inconsistent with the small amount of quenching if the singlet-triplet crossing is indeed the mechanism responsible for the abstraction component. In addition, the abstraction component (as well as the insertion component) for the reactions of $O(^1D)$ with RH produced OH with a statistical distribution in the spin doublets in contrast to the reactions of $O(^3P)$ where the lower spin doublet is populated by a factor of two over the upper one⁶⁰. Based on these results (insignificant quenching and the statistical population of the spin doublets) it does not appear that a singlet-triplet crossing can explain the abstraction component in these reactions.

The insertion component for these reactions was characterized by very high rotational excitation and greater than statistical vibrational excitation. The vibrational excitation decreased slowly with the number of carbon atoms ($P(v=1)/P(v=0)$ went from 1.0 for methane to 0.55 for propane) while the rotational excitation remained exceedingly high for all reactants (the rotational surprisal went from -6.5 for methane to -25 for cyclopentane). These results are consistent with a short-lived insertion intermediate in which the reaction exothermicity and collision angular momentum have insufficient time to dissipate to the remainder of the intermediate.

In the first section of this thesis, for the reaction $O(^1D) + H_2$, the trajectories could be categorized as either direct (zero or one times in the well) or indirect (two or more times in the well) and these two classifications exhibited different product distributions. A similar explanation of the two apparently different mechanisms in the alkane reactions (the high and low rotation components) does not seem appropriate. The high rotation component is consistent with a direct (short lifetime) insertion mechanism. The low rotation component cannot be attributed to an indirect (long lifetime) insertion collision complex for two reasons. Firstly, the low rotation component from the alkane reactions was colder⁵⁷ than expected from a long-lived, statistically governed complex and secondly, the trajectory calculations reported in the first section of this thesis did not exhibit any notable difference in the rotational distributions from the two types of collision complexes. It must be noted, however, that the two reactions being discussed, $O(^1D_g)$ with H_2 or with alkanes, are intrinsically different in that the other product in the H_2 reaction was an atom (H) which could not carry any of the angular momentum while that in the alkane reactions was a molecule which could. Despite this difference, it is difficult to envision a mechanism by which the OH fragment from a long-lived intermediate could have less than the statistically calculated angular momentum partitioned to it. As a result, the existence of two different mechanisms (insertion and abstraction) being responsible for the OH product in the alkane reactions appears to be correct.

The alternate product channels in the reaction of $O(^1D)$ with methanes must also be considered. These result from the substitution of an H-atom, and the elimination of H_2 or HX . Both of these channels result from the insertion of the O-atom into a C-H bond. One mechanism which could produce these channels requires a short-lived collision complex with sufficient reaction exoergicity being isolated in the newly formed H-O

bond (rather than C-O bond which leads to the OH product) to break it. The resulting H-atom then separates from the molecular fragment without further interaction resulting in the H-atom substitution channel or it can undergo a subsequent interaction with one of the other constituents of the molecular fragment resulting in the formation of H₂ or HX. The other mechanism by which these channels could be produced again requires insertion, however the collision complex exists sufficiently long for the reaction energy to dissipate from the reaction site and unimolecular decomposition of the unstabilized intermediate would produce these products with statistical distributions.

The branching ratios into these channels for the reaction of O(¹D) with methane have undergone considerable dispute. DeMore and Raper⁵⁴ found evidence of molecular elimination of H₂ when the reaction occurred in liquid argon. This observation was supported by the work of Cvetanovic and coworkers⁴⁷⁻⁵² on the higher alkanes in the gas phase. Bradley *et al.*⁶¹, however, attributed the presence of H₂ to a side reaction while Greenberg and Heicklen⁶² were unable to detect H₂. Lin and DeMore⁵⁶ measured the H₂ yield to be approximately 9% of the reaction with methane and the H-atom yield around 3%. Finally, in a molecular beam study of the reaction with methane⁶³ the branching ratio for H-atom substitution was found to be at least three times that of molecular elimination of H₂. Casavecchia *et al.*⁶³ considered their result to be in agreement with *ab initio* results for the H₄CO potential energy surface²⁹. The more exothermic H₂ molecular elimination channel was disfavored due to substantial barriers (393 kJ/mole for co-production of CHOH and 418 kJ/mole for CH₂O) while the less exothermic H-atom substitution channel encountered no exit barrier and was statistically favored. This agreement was based on the assumption that these two channels resulted from the unimolecular decomposition of the long-lived excited methanol formed by insertion of the O-atom. This assumption may not be valid (see below) nor is it

necessary for the molecular beam results to be correct. If, instead, a direct reaction is assumed for the H-atom substitution as the initial step for either of these channels, then a subsequent interaction with one of the remaining H-atoms would be required for the eventual H₂ molecular elimination. During the initial insertion, the C-H bond must extend to accommodate the incident O-atom. The subsequent removal of the H-atom would require further extension of the newly formed O-H bond which, combined with the translational energy imparted to the departing H-atom along the direction of the old bond, could inhibit further interaction with the relatively small, closely bound H-atoms of the CH₃O fragment. Thus, a direct (short-lived) insertion could also favor H-atom elimination over molecular elimination of H₂.

The analogous channels in partially halogenated methanes are H-atom substitution and HX molecular elimination: H₂ elimination can also occur as discussed in the previous paragraph if the halomethane contains two or three H-atoms. The initial step for either of these channels would be expected to be insertion of the O-atom into a C-H bond followed by either the prompt ejection of the H-atom with subsequent interaction with one of the halogen atoms in the molecular fragment to form HX or a long-lived collision complex which undergoes unimolecular decomposition into the channels under discussion. The initial distributions of the HX products from the reaction of O(¹D) with halogenated methanes has been studied⁶⁴⁻⁶⁹ and indicate that these different mechanisms (direct insertion and long-lived intermediate) may pertain for different molecular reagents.

Lin⁶⁵ and Aker *et al.*⁶⁹ studied the vibrational distribution of the HCl produced from the reaction of O(¹D) with CHCl₃ (by determining the appearance time of the laser emission and by time-resolved Fourier transform infrared detection of the resulting chemiluminescence respectively). Lin determined that the ratio of the two lowest

vibrational levels was $N_{v=1}/N_{v=0} = 0.5$ while Aker *et al.* measured the relative populations of levels $v = 1, 2$, and 3 to be $0.77 : 0.15 : <0.04$. Neither investigation determined the rotational distributions; Lin required rotational relaxation to a Boltzmann distribution for his calculations and the first observation time of Aker *et al.* was after 14 gas kinetic collisions at which time substantial rotational relaxation would have occurred. Combining the results of these two investigations and normalizing to $v = 0$ gives the vibrational distribution for the first four levels as $1.0 : 0.5 : 0.1 : <0.03$. This distribution is 'cold' and is what would be expected from a statistically governed unimolecular decomposition of an energetic insertion intermediate. The vibrational distributions from all of the other halogenated methanes studied were more excited than statistically expected which indicated a short-lived direct insertion mechanism. The results for these molecular reagents and the references pertaining to each are summarized below:

Reagent	Product	Vibrational Distribution	Reference
CH_2Cl_2	HCl	- : 1.0 : 0.76	65
CH_3Cl	HCl	1.0 : 0.61	65
CH_3F	HF	1.0 : 0.88 : 0.64 : <0.41	67
CH_2F_2	HF	1.0 : 1.02 : 0.99 : <0.45	68
CHF_3	HF	1.0 : 0.95 : 0.8 : <0.49	67
CHF_3	HF	- : 0.25 : 0.21 : 0.18 : 0.19 : 0.12 : 0.05	69
CH_2ClF	HF	- : 1.0 : 0.8	66
CHCl_2F	HF	- : 1.0 : 0.8	66
	HCl	1.0 : 0.5	66
CHClF_2	HF	- : 1.0 : 0.8	66.

The distribution for the HCl produced from reaction with CHCl_2F was not as 'hot' as those from the other reactions, although this result⁶⁶ is questionable since only one weakly lasing line was observed for this system.

Little is known about the rotational excitation of the HX produced in these reactions. The method of data analysis employed by Burks and Lin⁶⁸ required that complete rotational relaxation to a Boltzmann distribution be attained prior to the onset of HX laser emission. In the reactions with CH_3F and CH_2F_2 , a substantial addition of an efficient rotational relaxer (SF_6) was required to meet this criterion, indicating that the HF was originally produced with high rotational excitation. The only direct determination of the HX rotational excitation⁶⁹ was for the HF produced in the reaction with CHF_3 . Even though the first observation time by Aker *et al.* was after five gas kinetic collisions which would have afforded substantial rotational relaxation, the HF product still retained significant population in higher rotational levels of all vibrational levels observed. The occurrence of high rotational excitation coupled with 'hotter' than statistical vibrational excitation is incompatible with HX formation from a long-lived intermediate. The vibrational excitation of the HX products in these reactions indicates that the collision complexes are relatively short-lived with limited migration of the reaction exoergicity away from the reaction site to the remainder of the complex. The high rotational excitation (in the three reactions where it has been determined) indicates that the formation of the HX product takes place by a two-step process. The H-atom must be released from the collision complex first and subsequently interact with a halogen atom to ultimately form the HX product: if the H-atom and halogen atom leave the collision complex together in a single step very little rotation of the HX product would be expected. It has been suggested by Burks and Lin⁶⁸ that the degree of vibrational excitation is indicative of the lifetime of the collision complex. Those reactions with a higher density of states in:

the collision complex would undergo greater migration of the exoergicity to the remainder of the intermediate and would have a correspondingly longer lifetime with a more statistical distribution of the reaction energy into product vibration. This would account for the 'cold' vibrational distribution of the HCl from CHCl_3 since it would have the largest density of states of all the halogenated methanes under discussion. If a similar mechanism pertains in the reaction with CH_4 , the H-atom substitution and H_2 molecular elimination would proceed directly rather than by a long-lived intermediate which undergoes unimolecular decomposition as assumed by Luntz⁵⁷, as discussed previously.

An additional complication in the HX formation from halogenated methanes has been suggested by Aker *et al.*⁶⁹. In their study of the HX formed from reaction with CHCl_3 and CHF_3 , emission from CO was observed in the spectra obtained from the CHCl_3 reaction whereas none was apparent in those from the CHF_3 reaction. The amount of CO apparent in the CHCl_3 spectra was estimated to be approximately equal to the amount of HCl produced. In this reaction, two energetically accessible channels are available for the formation of HCl; one co-produces $\text{COCl}_2(X^1A_1)$ in its ground state and the other $\text{COCl}_2(A^1A'')$ in the first electronically excited state. The $\text{COCl}_2(A^1A'')$ excited state is, however, strongly predissociative (forming CO and Cl_2) and reaction along this channel would produce equal amounts of CO, HCl, and Cl_2 . In addition, reaction along this path is geometrically favored since the $\text{COCl}_2(A^1A'')$ state is bent with angles very close to those expected in the CCl_3OH intermediate whereas the $\text{COCl}_2(X^1A_1)$ ground state is linear and would require substantial realignment of the collision complex prior to product formation or that the $\text{COCl}_2(X^1A_1)$ be formed with a large degree of excitation in the bending mode. In the reaction with CHF_3 , the $\text{COF}_2(A^1A'')$ excited state is stable and no CO formation would be expected and none was observed in the spectra. The participation of the excited state channel was indicated, however, in the HF vibrational

distribution which decreased monotonically from $v' = 1$ to 3 and then had a slight secondary maximum at $v' = 4$. Reaction along the $\text{COCF}_2(\text{A}^1\text{A}'')$ channel is energetically capable of producing HF up to $v' = 4$ whereas the $\text{COCF}_2(\text{X}^1\text{A}_1)$ ground state channel is energetically capable of producing HF up to its dissociation limit (approximately $v' = 23$). The occurrence of an inflection in the vibrational distribution at $v' = 4$ and variations in the characteristics of the rotational distributions for the lower and higher vibrational levels was interpreted by Aker *et al.*⁶⁹ to be due to reaction into these two channels. Further corroboration that the excited carbonyl channel participates in the reactions of $\text{O}(^1\text{D})$ with halogenated methanes comes from the work of Lin⁶⁴⁻⁶⁶ and Burks and Lin^{67,68}: mass spectrometer analysis indicated the presence of large amounts of CO in all of the samples after reaction except for the CHF_3 reactant. This is in agreement with the known predissociations of the excited states of all the carbonyls (except COF_2 which is stable) resulting from these reactions.

One final point must be discussed in connection with the formation of HX from reaction with halogenated methanes; the measured branching ratio of OH to HX. This branching ratio has been determined by Aker *et al.*⁶⁹ for two of the halogenated methane reactions. In the reaction with CHCl_3 the OH/HCl ratio was estimated to be approximately 0.2 and for CHF_3 the OH/HF ratio to be less than 0.8. These ratios are difficult to reconcile with the assumed mechanism for HX production. Insertion of the O-atom into the C-H bond has been assumed to lead to both of these channels (with abstraction being an additional mechanism for OH production). In the reaction with CH_4 , OH production has been measured⁵⁶ to be about 80% with 40% of this resulting from the insertion mechanism while H-atom substitution and H_2 molecular elimination accounts for approximately only 13.5% of the reactivity. It is difficult to understand why OH formation is substantially disfavored over H-atom substitution (and eventually HX production) in these triply

halogenated methanes. This point will be returned to in the discussion at the end of this section.

The remaining reaction site is at the C-X bond and it is the least studied to date. Addison *et al.*⁷⁰ studied the reaction of O(¹D) with CHClF₂ and found that ClO production accounted for 55% of the reaction and considered direct abstraction of the Cl-atom by the the O-atom to be the mechanism responsible. This high reactivity at the halogen site is supported in the reaction with CF₃Cl, CF₂Cl₂, and CFCl₃ where ClO production was determined⁷¹ to be greater than 33%, 40%, and 33% respectively. There have been no determinations of the vibrational or rotational distributions of the halogen oxide product. The only other studies⁴¹⁻⁴⁶ that relate to reaction at this site are for the reaction of singlet methylene, CH₂(a¹A₁), (which is isoelectronic with O(¹D)) with singly chlorinated alkanes. In all of these studies, reaction of singlet methylene with the Cl-atom was found to be exclusively by abstraction. In addition, the presence of the Cl-atom reduced the amount of insertion into C-H bonds, even on adjacent C-atom⁴⁶.

II.A.2. Apparatus

The reaction of $O(^1D_g)$ with various halogenated methanes was carried out in a low-pressure reaction chamber. The product chemiluminescence within the range of approximately 2000 to 4000 cm^{-1} was observed by time resolved Fourier transform spectroscopy. The interferograms thus obtained were stored and subsequently Fourier transformed to produce spectra. These spectra were analysed to determine the population of individual rovibrational levels and thus the early vibrational distribution of the products observed.

The O^* precursor, ozone, was produced in our laboratory prior to each day of data taking, requiring a minimum of 24 hours to produce a sufficient quantity (approximately 5 moles) for a normal day's run. Ozone was produced by the silent-arc method, in which a constant low flow of oxygen (Air Products, zero grade) at atmospheric pressure, that had been purified by passing it through a Linde type 5A molecular sieve kept at 195 K, was passed over tungsten electrodes between which a 15 KV AC discharge was maintained. The ozone thus produced was trapped and stored on silica gel maintained at 195 K by circulating cooled methanol around the glass storage cylinders. When the ozone was used, the storage cylinders were isolated from the generator section and the excess oxygen pumped off until a pressure of about 5 Torr remained in the storage cylinders. During the experimental runs, the ozone was desorbed from the storage material by its own partial pressure. Its flow was maintained (but not measured) by opening six teflon valves such that the pressure of ozone in the reaction chamber remained constant at the required value, as indicated in the description of the individual reactions.

The halogenated methanes, CH_3F (SCM Specialty Chemicals, research grade), CHClF_2 (Matheson, research grade) and CH_3Cl (Matheson, research grade) were used without

further purification. The flow of each gas was measured using Matheson Tri-flat flowmeters and kept constant by monitoring the pressure in the reaction chamber with an MKS Systems capacitance manometer. The ozone and halogenated methane were usually used with equal partial pressures which were attained by establishing the pressure of one of the reactants in the chamber and then increasing the flow of the second until the total pressure was twice that of the first. The pressures were monitored periodically throughout a run (while the interferometer was temporarily halted) by first terminating the flow of one and then the other and checking the partial pressure of each.

Ozone and the molecular reactant were admitted to the reaction chamber by two concentric, teflon-coated quartz tubes mounted on vacuum seals in the centre of the lid of the reaction vessel shown schematically in figure 29. The ozone flowed through the outer (2.5 cm diameter) tube and the halogenated methane through the inner (0.5 cm diameter) injector tube. Efficient mixing was ensured by suspending a teflon deflector disc 0.1 cm below the tip of the injector and by vertically translating the injector such that the point of reagent mixing was not more than 0.5 cm below the end of the outer tube. This afforded efficient mixing of the reagents as well as minimizing collisional relaxation of the products.

The reaction vessel consisted of a 25 cm diameter stainless steel cylinder that was 25 cm high. Eight rectangular ports were welded at equal distances around its circumference to afford attachment of pressure sensing devices and optical components. The reagents were continuously evacuated at the bottom of the vessel by a Varian VHS 400 diffusion pump backed by an Edwards blower and mechanical booster. The diffusion pump was connected to the chamber by a 38 cm diameter cryobaffle, maintained at 200 K by the circulation of cooled methanol, and a 30 cm adjustable gate valve. To reduce the

Figure 29: Vertical cross-section of the reaction chamber.

consumption of reagents the gate valve was typically throttled during the experiment to maintain a pumping speed of approximately 300 litres per second. This pumping speed ensured that the reaction chamber volume was swept clean of products between laser pulses. The lid of the reaction vessel supported the reagent inlet tubes and held a liquid reservoir through which circulated methanol cooled to 200 K. Four copper vanes, about 10 cm wide and 15 cm deep, were attached to the underside of the lid and was used as a light baffle and to absorb the large amount of heat resulting from the laser photolysis.

$O(^1D_g)$ was generated from ozone by laser photolysis at 248 nm. The laser pulse was from a Lumonics model TE-860 excimer laser operated with a KrF gas mixture. The maximum average power that could be obtained from the laser was 8.5 Watts when operated at about 330 Hz, as required for optimum data acquisition (*vide infra*). The laser beam was approximately 1 cm high by 2 cm wide and entered the reaction chamber horizontally, figure 29. The position of the laser beam was vertically adjusted so that its top edge just missed the bottom of the reagent inlet tubes, and its bottom edge passed just above the top of a dielectric mirror situated inside the reaction chamber next to its quartz entrance window. The laser beam traversed the reaction chamber and was reflected from another dielectric mirror on the opposite side of the reaction chamber, back to the mirror next to the entrance window, with the top of the laser beam incident at the top of this latter mirror. Both dielectric mirrors were coated for maximum reflectivity (around 95%) at 248 nm. The two mirrors were adjusted to cause the laser beam to pass four times through the cavity before exiting at the same point where it entered.

The absorption coefficient for ozone⁷² at 248 nm is approximately $265 \text{ atm}^{-1} \text{ cm}^{-1}$ at 298 K base e. For the pressures used in these experiments (typically 5 - 10 mTorr), with the above mentioned laser power and four passes of the laser beam, almost complete

photolysis of the ozone along the laser's path was accomplished. The photodissociation of ozone at 248 nm produces:

The quantum yield of O^* at this wavelength is approximately 88%, with 5.18 and 4.46 kcal/mole of energy partitioned into vibration and rotation, respectively, of the $\text{O}_2(^1\Delta)$ molecular fragment⁷³.

The observed chemiluminescence from the products was collected by a Welsh-type multipass optical system whose optical axis was horizontal and perpendicular to the direction of the photolysis laser beam. The configuration of the optical components is depicted in figure 30. The Welsh-type cell consisted of four paired spherical concave gold coated first-surface mirrors, approximately 6 cm high and 3 cm wide each, situated at either side of the reaction chamber (at a separation of approximately 8 inches) and positioned such that the top of the mirrors were at the same height as the top of the photolysis laser beam. They were aligned to collect infrared emission originating between them and focus it to a point at the centre of a gap between the pair closest to the interferometer. Prior to each experiment the Welsh cell was positioned vertically by reflecting a helium-neon alignment laser backwards through the interferometer and aligned by means of a diffuse white light positioned at the aperture of the interferometer. The fine adjustment of the horizontal position of the Welsh cell was accomplished at the start of each experimental run by maximizing the detector signal. The Welsh cell mirrors were removed, stripped and recoated after two or three days of data collection to ensure maximum efficiency. Emission from the Welsh cell was coupled to the interferometer by an $f/1$ CaF_2 convex lens.

Figure 30: Horizontal cross-section of the reaction chamber.

The emission from the Welsh cell was recorded by a Nicolet 7199 Fourier transform infrared spectrometer. It consisted of a scanning Michelson interferometer with a CaF_2 beamsplitter, coated for approximately 4000 to 1500 cm^{-1} , and had a resolution of approximately 1 cm^{-1} for the scan parameters used for all three experiments. The light from the interferometer was focused onto a 1 mm^2 InSb detector cooled to 77 K. The signal from the detector was amplified and electronically filtered before it was passed to the data acquisition processor. The bandpass of the filters was typically 1 Hz to 100 KHz which gave a detector risetime (to the 90% value) of approximately $1.3\text{ }\mu\text{sec}$ which was adequate to observe the infrared signal which typically had a risetime around $20\text{ }\mu\text{sec}$.

During the course of these experiments, two different data acquisition procedures were used, as will be described in the next sub-section. For the experiments with CHClF_2 , the amplifiers, filters, and analog-to-digital converter of the Nicolet 7199 Fourier transform infrared spectrometer as well as a Nicolet 1180 computer (for data storage and manipulation) were used. The interferograms for the other two experiments reported in this thesis were collected using alternate data acquisition electronics. In these latter measurements the Michelson interferometer of the Nicolet 7199 FTS was still used, but the detector signal bypassed all of its signal handling electronics. The detector signal was processed by an Ithaco amplifier-filter and then digitized by a LeCroy 8818 8-bit, 100 MHz transient recorder and stored using a DEC LSI 11/83 computer onto an Emulex winchester.

II.A.3. Data Acquisition and Analysis

The data in the experiments were obtained by two (slightly different) implementations of time resolved Fourier transform spectroscopy. The method used for CHClF_2 has been used in this laboratory for several experiments and has been fully described elsewhere⁷⁴. For CH_3F and CH_3Cl the implementation was made more efficient by enabling several time-delayed spectra to be recorded for each transient. A general description of the latter implementation can be found in references 75 and 76. For the purposes of this thesis, only a brief outline of the data acquisition methods employed will be given.

A schematic of the data acquisition system for CHClF_2 is given in figure 31. The system computer (Nicolet 1180) controlled all routine operations of the interferometer, such as scan length, velocity, and signal manipulation, as well as handling assessment and storage of the interferograms. The timing computer (LSI 11/23) provided the time resolution for the experiment. The essential aspects of the time resolution are given in figure 32. In essence, the timing was accomplished by initiating the transient (the infrared emission) when O^* was 'instantaneously' produced by the short (about 10 nsec) photolysis laser pulse at a preset time (τ_d) prior to the acquisition of each data point. The data points were taken at each zero-crossing of a reference HeNe laser in the interferometer. Thus each successive data point represented an optical path difference of one half of the wavelength of the HeNe laser, or, alternatively, the time between each point was one half of the period of the HeNe laser. This resulted in a data acquisition rate of 1 KHz for the fixed speed that was used for the scanning mirror. The excimer laser had a maximum usable repetition rate of 330 Hz, which meant that only every third data point could be detected in a single scan. Thus, three complete scans were collected to obtain a single interferogram. The only timing errors inherent in this method were the

Figure 31: Block diagram of the apparatus.

Figure 32: The relative timing for time resolved data acquisition by the Nicolet 1180 Fourier transform infrared spectrometer.

results of variations in the mirror velocity, which was about $\pm 5 \mu\text{sec}$, and jitter in the laser firing, which was only a few nanoseconds.

In the second implementation, the data points were digitized by a transient recorder controlled by an LSI 11/83 computer. The time resolution was accomplished in much the same way as in the previous system, with one essential difference: for each transient, up to fifteen time delays were collected, as depicted in figure 33. This permitted the acquisition of fifteen time delays in the length of time the previous system required to take one. In addition, the present system monitored the power of the excimer laser and scaled each data point accordingly. This further reduced the time required to complete an experiment by reducing the noise induced in the spectra due to variations in the laser power.

The signal-to-noise was improved in both systems by coadding many interferograms. In the single time delay system, the smallest number of coadditions was 140 and the largest number was 1010, requiring a total of six days of data collection to obtain only five time delays. The multiple time delay system coadded the same number of interferograms for all time delays (due to all delays being collected in the same scan). For CH_3F , 533 coadditions were performed in two days producing fourteen time delays, and for CH_3Cl 1393 coadditions were required, taking five days and again resulting in fourteen time delays. This illustrates the significant reduction in experiment time afforded by the multiple time delay system.

The interferograms for CHClF_2 were transformed and analysed using software resident on the Nicolet 1180. The interferograms for CH_3F and CH_3Cl were first stored on a winchester accessed by the LSI 11/83, transported via floppy disc to an IBM 370 located at the National Research Council of Canada Computing Services, and finally archived on

Figure 33: The relative timing in the data collection implementation by which several interferograms were collected concurrently.

9-track tape. They were transformed and analysed using FORTRAN programs written for the IBM 370.

All interferograms contained 16384 data points and were processed in the same way. The zero path difference region (ZPD) was zeroed to eliminate baseline curvature in the transformed spectra (due to the broad continuum arising from blackbody emission from optical components at room temperature) and then apodized with a Happ-Genzel function. They were transformed using the Cooley-Tukey Fast Fourier transform algorithm⁷⁷ (the FORTRAN program for the IBM 370 utilized a Fourier transform package obtained from the SLATEC library⁷⁸) and power spectra were obtained (necessitated due to the loss of phase information during zeroing of the ZPD).

Analysis of all spectra were the same also. The spectra were corrected for detector response and changes in transmissivity of the optical components through division by a reference file. The method by which the reference file was obtained is explained in reference 79.

The instrumental linewidth for all spectra was approximately 1 cm^{-1} , which in all cases was greater than the Doppler width (around 10^{-4} cm^{-1}) of the emission lines. As a result, the emission intensity of individual rovibrational states could be related directly to the population of the states (without regard for the lineshape of individual lines) by the relation:

$$I^{v'J'}_{v''J''} = P(v'J') * A^{v'J'}_{v''J''} \quad 2$$

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

The line positions and A-factors used for the analysis were as follows: line positions for OH($X^2\Pi$) from the AFGL trace gas compilation⁸⁰ (1982 version), for HF($X^1\Sigma^+$) and HCl($X^1\Sigma^+$) from term value expansions⁸¹. The A-factors for OH were from the calculations of Langhoff *et al.*⁸², for HF from the transition moments calculated by Oba *et al.*⁸³ using the dipole moment function of Sileo and Cool⁸⁴ and HCl from the transition moments calculated by Oba *et al.*⁸³ using the dipole moment function of Ogilvie and Tipping⁸⁵. The Fortran population analysis programs were written by the author, one for analysis of hydrogen halides and one for OH (which required a more detailed accounting of lines due to the two spin states (E-states) and the Λ -type doubling of each rotational level).

In the analysis program, populations were determined for all emission lines with S/N greater than 1 (determined manually). A listing of the OH analysis computer program (the more complex of the two) is given in appendix A.2. Basic information about the spectrum to be analysed was read in first, *ie.* file name, product identity, and the specification of all spectral lines to be analysed (given by upper vibrational level, branch identification, and range of (lower) rotational levels). Next, the spectrum was prepared for analysis; laser 'glitches' were removed and the spectrum was corrected for the detector response. The transition library, containing wavenumbers and A-factors for the molecule to be assigned, was read in and each line which matched one of those to be analysed for was identified and stored in a secondary library where it was specified by consecutive numbers in the listing. This secondary library was then sorted into a four parameter array in which the four parameters specified the v level, J level, branch and E-state/parity. The elements of this 'sort' array were the numbers of the lines in the secondary library. In this way, the pertinent information about any spectral line could be quickly found simply by specifying its four parameters. The final step before the actual

analysis was to identify lines that were overlapped so they could be deconvoluted during analysis. Lines which lay within twice the instrumental resolution of each other were considered to be overlapped. Each line in the secondary library was assigned an 'overlap vector' in which its number of overlaps was specified along with the identifying numbers of each overlapping line from the secondary library. The program was capable of handling up to 5 overlaps, although this number was never required for the results of the next sections (a maximum of 3 overlaps was encountered and this occurred only in the somewhat more congested HF spectrum from CH_3F at the first time delay). The heights of the individual spectral lines were measured from their local baselines, and the error in each line was defined as half of the local noise. The population of individual lines was determined by the relationship in equation 2. Note, the spectra were for the detector response (power) as a function of wavenumber not intensity so the population of a line had to be divided by the wavenumber of that line to be properly scaled. Overlapped lines were deconvoluted by solving the matrix equation relating the true line heights to the measured line heights assuming a Gaussian line shape. The calculated populations and their errors were stored, and the populations for each vibrational level, each branch and the total population for each E-state were calculated. The error for each of these was taken as the square root of the sum of the squares of the error in each contributing rotational level. All the calculated populations and their errors were output into a permanent file (on disc) for future use.

For all molecules, only the P-branch ($J' - J'' = -1$) was analysed for each state since its A-factors are significantly larger than those of the R-branch ($J' - J'' = 1$), and the Q-branch ($J' - J'' = 0$) of OH was severely overlapped. In addition, only the $3/2$ spin state of OH was used for determining populations even though the $1/2$ state was also analysed. The $3/2$ state has greater intensity due to the statistical weight of this state as opposed to that

of the $1/2$ spin state. This gave smaller errors in the populations determined from the $3/2$ state. The OH λ -doublets were overlapped for most of the rovibrational levels observed in these experiments and an average value for the two was assigned as the population of each rovibrational level.

In some spectra, portions of some of the R-branches had to be included to properly handle overlaps, although the calculated populations from these R-branches were later disregarded.

II.B. Results: Experimental

II.B.1. $O(^1D_g) + CH_3Cl$

II.B.1.a. Overview: $O(^1D_g) + CH_3Cl$

The reactive channels, pertinent to this investigation, for the reaction of O^* with CH_3Cl are:

The only products from this reaction which had rovibrational bands situated in the range of the detector and had sufficient intensity to be observable were HCl, CO and OH, occurring in reactions (2a) to (2e) and (2h). Reaction (2b), even though it had the same products as reaction (2a), was considered as a separate channel since it had different

energetics and was expected to have different dynamics since the geometries and potential surfaces of the (X^1A_1) and (A^1A'') states of CH_2O differ. The $CH_2O(X^1A_1)$ ground state is planar with C_{2v} symmetry while the A^1A'' first excited state is bent (C_s symmetry) with the O-atom at an out-of-plane angle of 31° . Despite the smaller exothermicity of reaction (2b) it was expected to compete efficiently with the more exothermic channel (2a) since it more closely resembled the expected geometry of the transition state for these two channels. Reaction (2c) to (2e) were expected to be predominantly due to the predissociation of the $CH_2O(A^1A'')$ state rather than fragmentation or unimolecular decay of the collision complex. The remaining reactions (2f,g,i,j) to (2i) were not directly observable but were pertinent to the discussions below.

Davidson *et al.*⁸⁶ analysed the rate constants for deactivation (reaction and quenching together) of O^* with eleven different halogenated methanes or ethanes and devised a simple scheme based on bond additivity (similar to the correlation between reactivity and number of C-H bonds found for saturated hydrocarbons^{55,87}) by which these rates could be calculated. The branching ratio of each bond into reaction and quenching, however, was not determined. Davidson *et al.* found that the deactivation rates studied were well approximated by the expression:

$$k(C_nH_aF_bCl_c) = (a*0.32 + b*0.03 + c*0.74) * 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad 3$$

where n, a, b, and c represent the number of C, H, F, and Cl atoms in the molecular reagent respectively. The validity of this expression has not been suitably verified, and has, in fact, been disputed⁵⁹. Force and Wiesenfeld⁵⁹ measured the direct contributions of both reaction and quenching to the deactivation rate of O^* for eleven halomethanes by monitoring the time profile of the absorbance at 130 nm ($O(3^3S_1 \leftarrow 2^3P_j)$) as a function of molecular reagent pressure. Their deactivation rates that they found agreed, generally,

with the calculated rates of Davidson *et al.*⁸⁶, with the exception of CHF_3 and CF_4 . These were substantially lower, 0.084 and $0.0018 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ respectively, than any previous determinations - for example, Fletcher and Husain⁸⁸ measured the deactivation rate constants to be 0.4 and $0.12 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for these molecules. From their experimental rates, Force and Wiesenfeld determined that the ratio of $k(\text{CH}_4)/k(\text{CHF}_3)$ was 19 whereas the upper limit for this ratio would be 4 (with no contribution from the C-F bonds) based on bond additivity. Since their deactivation rate for CHF_3 was substantially lower than the previous determination⁸³, this was not considered sufficient grounds to discount equation 3. Bond additivity in the form of equation 3 was considered too useful for estimating branching ratios to discount because of these discrepancies particularly since the rates determined by Force and Wiesenfeld for these two reactions differed from previous determinations.

No single investigator has experimentally determined the reaction rates for O^* with all three halogenated methanes reported in this thesis. The exact magnitude of the individual reactions were considered to be of less significance than their relative values. The calculated values obtained with equation 3 were used for all three reactions reported here as these values were sufficiently accurate and gave a better indication of their relative magnitudes as opposed to comparing values from different sources. The reaction rate for $\text{O}^* + \text{CH}_3\text{Cl}$ calculated from equation 3 was $1.7 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. This value was in adequate agreement with the value of $2.1 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (90% reaction, (2a) to (2j), and 10% quenching, (2k)) found by Force and Wiesenfeld.

The reactive branching ratios (reactions (2a) to (2j)) have not been studied to date. Addison *et al.*⁷⁰ studied the reaction of O^* with several halogenated methanes (of which, only CHClF_2 is common between that study and this) and found that a major reactive

channel was abstraction of a halogen atom - approximately 55% for $O^* + CHClF_2$. This finding was in agreement with that of Gillespie and Donovan⁷¹: in reactions of O^* with halomethanes of formula CF_xCl_y , chlorine abstraction accounted for over 30% of the reaction. Similar results were obtained by Bamford and Casson⁴⁶ in a study of singlet methylene (which is isoelectronic with O^*): reaction with a C-Cl bond was greatly favored over reaction with a C-H bond on the same or even the adjacent C-atom. From the bond contributions indicated in equation 3, reaction (2i) could be a major channel only if reactions (2a) to (2e) and (2j) (molecular elimination of HCl and Cl substitution) had very small branching ratios. The three C-H bonds contributed $0.96 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ to the deactivation rate by quenching (2k) and in the formation of HCl, H_2 , H, and OH in reactions (2a) to (2h). The single C-Cl bond contributed $0.74 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ to quenching (2k) and the formation of HCl, ClO, and Cl in reactions (2a) to (2e) and (2i,j). The individual contributions of the bonds to quenching (2k) were unknown and this channel was ignored since it had been measured⁵⁹ to be only 10% of the total deactivation rate. Three of the reactive channels, (2f), (2g), and (2j), were considered to contribute very little to reaction in analogy to the reaction of O^* with CH_4 . Hydrogen elimination, both atomic and molecular (reactions (2f) and (2g)), were both results of H-atom substitution when the O^* inserted into a C-H bond. In the analogous reaction of O^* with CH_4 , these two channels were found to contribute only about 13% to the overall reaction rate⁵⁶, although their separate contributions are still debated. In a gas phase study, Lin and DeMore⁵⁶ found that formation of H_2 contributed 9% to the CH_4 reaction while H-atom elimination was a minor channel (less than 3%). Alternatively, Casavecchia *et al.*⁶³ in a molecular beam study of the $O^* + CH_4$ reaction found that the ratio of H-atom substitution to molecular H_2 elimination was greater than 4. From these studies of the CH_4 reaction, it was expected that OH production in the

reaction with CH_3Cl would again dominate over H-atom substitution or H_2 molecular elimination. It was unknown how well HCl molecular elimination would compete with H_2 molecular elimination, however from the relative bond energies⁸⁹ of C-Cl and C-H bonds (358 and 405 kJ/mole respectively) in a chlorinated methane and the bond lengths⁹⁰ in CH_3Cl , it was expected that HCl elimination would exceed that of H_2 . In addition, the relatively large size of the Cl-atom would promote interaction between it and the expelled H-atom (as opposed to no interaction or interaction with the smaller H-atoms in the CH_2ClO co-product), thus making HCl elimination dominant over either H_2 elimination or H-atom substitution. Cl-atom elimination, reaction (2j) was found⁷⁰ to be less than 10% in the reaction of O^* with CHClF_2 and, again, was not expected to have a greater contribution in reaction with CH_3Cl . This was supported by the observed mechanism⁴³ in the reaction of singlet methylene with CH_3Cl in which insertion into the C-Cl bond (a prerequisite for Cl substitution) did not occur: reaction of singlet methylene with the C-Cl bond in chlorinated alkanes was entirely by Cl abstraction. Therefore, it was considered that the C-Cl bond contributed only to formation of HCl and ClO. HCl was common to both bond contributions (C-H and C-Cl) which hindered qualitative deductions from equation 3. If only small amounts of HCl were produced, then the C-H bonds contributed almost entirely to formation of OH and the C-Cl bond produced predominantly ClO (thus ClO would be a major channel). Alternatively, if HCl was produced in large amounts, then the C-Cl bond and C-H bonds both contributed substantially to its formation and very little ClO or OH would be formed. Measurement of the ratio of OH to HCl or ClO to HCl would substantiate whether or not production of ClO was a major channel.

Lin⁶⁵ carried out the only previous investigation of the dynamics of this reaction. In that experiment O_3 was flash-photolysed in an optical cavity in mixtures of different

chloromethanes and SF_6 (required for rotational relaxation of the product since the numerical expression for the gain assumed a Boltzmann rotational distribution). The HCl laser emission from the rovibrational levels produced in the reaction was observed and from the appearance times of the different laser lines the population ratio of the vibrational levels involved was calculated. Lin found that the ratio of the populations in the two lowest vibrational levels of HCl was $N_1/N_0 \approx 0.61 \pm 0.05$. The system used had insufficient time resolution to determine whether this was an upper or lower limit. The photolysis flash was quite broad, with a duration time of approximately 12 μs and peaked approximately 6 μs after the start of the flash. The onset of HCl laser emission occurred just prior to this peak. The total pressure used was 30 Torr, with an SF_6 partial pressure of approximately 27.3 Torr and 1.36 Torr each of O_3 and CH_3Cl . The total pressure was optimized to give maximum gain without apparent vibrational relaxation. This assumption (insignificant vibrational relaxation) was not borne out by a qualitative analysis of the experimental conditions. The appearance time of the first line to lase was 4.4 μs which represented around 860 gas kinetic collisions for the HCl produced at the beginning of the flash (780 collisions with SF_6 and 40 collisions with each of O_3 and CH_3Cl). As the flash intensity increased, the amount of HCl produced also increased until the gain, which is a function of the ratio N_v/N_{v-1} , was sufficient to initiate lasing. The HCl produced later in the flash would undergo correspondingly fewer collisions than that produced at the beginning of the flash, but the majority of the HCl that contributed to the emission would still have had many collisions with SF_6 and several collisions with each of O_3 and CH_3Cl . The SF_6 was chosen for its efficiency at relaxing the HCl rotationally while being inefficient at vibrational relaxation; SF_6 has a small cross section for vibrational relaxation of HCl ($5.5 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for $v' = 0 \leftarrow 1$)⁹¹ which decreases with increasing vibrational level (on the order of $1 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

for $v' = 1 \leftarrow 2$). On the other hand, CH_3Cl has a large cross section for vibrational relaxation of HCl which increases notably with vibrational level ($k(1 \leftarrow 2) = 9.5 * 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ to $k(4 \leftarrow 5) = 1.7 * 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)⁹¹. The cross sections for vibrational energy transfer in HCl by O_3 have not been measured but should be similar to those for CO which has a vibrational band close to the $2\nu_1$ and $\nu_1 + \nu_3$ bands of O_3 which are expected to be responsible for the V-V energy transfer from HCl.

The vibrational relaxation rates were easier to use when converted to deactivation probabilities per gas kinetic collision, *ie.*, each rate was divided by the average gas kinetic collision rate (the rigid sphere rate for a gas kinetic collision of HCl in 1 atmosphere of O_3 and CH_3Cl at equal partial pressures at 300 K was $1.83 * 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$). In this terminology, the estimated probabilities for deactivation of $v' = 1$ in Lin's results⁶⁵ by $\text{SF}_6/\text{CH}_3\text{Cl}/\text{O}_3$ were 0.003/0.032/0.0023 per gas kinetic collision (where the experimentally undetermined $k(0 \leftarrow 1)$ value for CH_3Cl was obtained by extrapolation using the measured rates for the higher v -levels and the O_3 value equated to that for CO). Multiplying the SF_6 value by 20 to reflect the ratios of the partial pressures (20:1:1) and summing these probabilities gives a total probability of 0.095 for deactivation of $\text{HCl}(v'=1)$ per gas kinetic collision. Similarly for $v' = 2, 3, 4$ and 5, the deactivation probabilities are 0.069, 0.18, 0.63, and 1.03 per gas kinetic collision. The similar value for the deactivation from $v' = 1$ and 2, and the rapid increase with vibrational level makes the population distribution at the onset of lasing very dependent on the time profile of the photolysis flash and the nascent distribution from reaction. A long flash permits the HCl from the start of the flash to be substantially relaxed while that produced later in the flash is partially relaxed, predominantly from the higher levels. In addition, if the nascent distribution is reasonably flat, either $v' = 1$ or 2 could form a blockage to relaxation and distort the distribution from the initial one. Due to the

uncertainty in the actual extent of relaxation, Lin's result can only be used as a guideline. In addition, Lin found large quantities of CO and CO₂ as well as CH₂O when a mass spectrometric analysis of the flashed mixture was performed.

II.B.1.b. Experimental Results: O(¹D_g) + CH₃Cl

There were fifteen time delays in all taken for each of the three reactions reported in this section. The 'zeroth' time delay was taken approximately 17 μs prior to the laser pulse which initiated reaction to verify that there were no (detectable) products left in the reaction chamber from the previous laser pulse. The first time delay was taken approximately 21 μs after the laser pulse (i.e., 21 μs after the reaction was initiated) and successive measurements were taken about every 38.5 μs thereafter. The last time delay was approximately 520 μs after the laser fired. Since the laser fired every 3000 μs, there was over 2400 μs between the last data point and the next initiation of reaction during which time the reaction chamber was pumped clear of products. Close scrutiny of the zeroth time delay (which was taken 17 μs before the laser fired) showed no discernible emission from the detectable products, confirming that the reaction chamber was suitably cleared between successive laser firings.

The O₃ and CH₃Cl had equal partial pressures of 10 mTorr each. The earliest time at which HCl emission was measured was 21 μs (the first time delay) after the reaction was initiated (by the laser photolysis of O₃), corresponding to an average of 2.7 gas kinetic collisions by the time of observation. The average collision frequency ($\bar{c}$) of a particle of species 1 with the particles of species 2 which has a partial pressure of P₂ is given by the expression⁹²:

$$\bar{c} = \bar{v}/\lambda_{1,2} = (8kT/\pi M_1)^{1/2} * \pi (\xi_1 + \xi_2)^2 P_2 (1 + M_1/M_2)^{1/2} / 4kT \quad 4$$

where $\bar{v}$ is the average velocity, λ is the mean free path, T is the temperature, M is the molecular weight and ξ is the molecular diameter. The average number of gas kinetic collisions $\langle Z_{\text{gk}} \rangle$ is given by:

$$\langle Z_{\text{gk}} \rangle = (\bar{c}_1 + \bar{c}_2) * t_n \quad 5$$

where t_n is the time of observation, i.e. the time of the n 'th time delay and $\bar{c}_1$ and $\bar{c}_2$ are the average collision frequencies for the product with the two major components of the ambient gas (in this case, the unphotolysed O_3 and the unreacted molecular reagent CH_3Cl).

For traces of HCl in the unreacted CH_3Cl and unphotolysed O_3 at partial pressure of 10 mTorr each (assuming a negligible amount of each has been consumed in the reaction), the combined collision frequency is $1.3 * 10^5 \text{ s}^{-1}$. Therefore, after 21 μs (the first time delay) the HCl had collided, on the average, 1.7 times with either a CH_3Cl or O_3 molecule, assuming that, on the average, for a reaction that is approximately gas kinetic, one collision was required to form the HCl . The earliest time at which OH emission was measured was 59.5 μs , corresponding to an average of 7.6 gas kinetic collisions prior to observation (where its average collision frequency in the unreacted CH_3Cl and O_3 was $1.44 * 10^5 \text{ s}^{-1}$) and again assuming that one collision was required for its formation.

Sample spectra obtained for this reaction are given in figures 34 and 35. The spectra in figure 34 were taken at approximately 8 (bottom), 24, 45 and 72 (top) average gas kinetic collisions (where these values represent an *average* for the two detected products, $(\langle Z_{\text{gk}} \rangle_{\text{HCl}} + \langle Z_{\text{gk}} \rangle_{\text{OH}}) / 2$). The emission from HCl is towards the left of each spectrum and that from OH towards the right. Individual lines can be identified by using the

Figure 34: Sample HCl and OH emission spectra from the reaction $O^* + CH_3Cl$ for approximately 8 (bottom), 24, 45, and 72 (top) gas kinetic collisions of the HCl or OH with the ambient gas in the reaction chamber. The templates at the top of the figure identify the rovibrational lines of HCl, towards the left, and OH, towards the right, as explained in the text.

1P 13 12 11 10 9 8 7 6 5 4 3 2 1 0 1 2 3 4 5 6 7 8 9 10 11 12 13 1R
 2P 7 6 5 4 3 2 1 0 1 2 3 4 5 6 7 2R
 3P 7 6 5 4 3 2 1 0 1 2 3 4 5 6 7 3R
 4P 3 2 1 0 1 2 3 4 5 6 7 4R

Figure 35: Sample CO emission spectra from the reaction $O^* + CH_3Cl$ for approximately 8 (bottom), 24, 40, and 56 (top) gas kinetic collisions of the CO with the ambient gas in the reaction chamber. The template at the top of the figure identifies the rovibrational lines of CO.

template at the top of the figure. The sequences at the left identify the HCl lines; five vibrational levels are indicated for the P branch and four for the R branch with a maximum denoted J level of 15. Spectroscopic notation is used throughout this thesis to indicate individual lines *ie.* νB_J where ν indicates the vibrational quantum number of the upper (emitting) state, B denotes the branch (P for $(J+1 \leftarrow J)$, Q for $(J \leftarrow J)$, and R for $(J \leftarrow J+1)$), and J indicates the relative ordering of the lower (final) rotational states, 0 for the lowest state, 1 for the next higher etc. For a molecule whose rotational levels are approximately those of a rigid rotor (such as HCl and HF) J is also the rotational quantum number of the lower (final) state. The OH emission lines are identified in the template at the right of the figure for the first four emitting vibrational levels for both the Q and P branches with nine rotational lines indicated for the P branch of each vibrational level. The Q branch is indicated by the position of the νQ_0 line only for each vibrational level since it was not resolved for any vibrational level with the resolution used in this study and higher J lines for the Q branches of OH have rapidly decreasing Einstein A coefficients and therefore have decreasing contributions to this spectral feature.

The power of the excimer laser varied from shot to shot by as much as 20%. This resulted in considerable fluctuation in the detector signal and noise level from one point to the next in the interferograms despite signal averaging. Since this fluctuation occurred with a frequency equal to that at which the laser fired and had components from all of its harmonics, Fourier transforming the interferograms resulted in 'spikes' or 'glitches' occurring at wavenumbers equal to $f/2v$, where f is the frequency at which the laser fired and v is the velocity of the moving mirror, and all of its harmonics⁹³ which were aliased into the region of observation. A more comprehensive discussion of this problem can be found in reference 94. Four such 'glitches' are present in the spectral region of figure 34 (around 2635, 3100, 3365, and 3595 cm^{-1}) and were clipped (the detector signal for the

data points in the spectrum over the width of the glitch were assigned a value close to the baseline in that region) for the purpose of both analysis and presentation. The laser glitches and their subsequent clipping affected only the few spectral lines that they overlapped. The spectral lines that were obscured by the laser glitches were assigned values during analysis by spline interpolation from adjacent lines.

The four spectra in figure 35 display the CO emission detected from the reaction of O^+ with CH_3Cl . These spectra are of very poor quality not only due to the small emission signal but also due to absorption of parts of the CO emission by 'hot' bands of O_3 ($000 \leftarrow 002$ and $000 \leftarrow 101$) that extend from around 1950 to 2160 cm^{-1} . As a result of the O_3 absorption, the only reasonably unaffected section of the CO spectrum was the 1R emission lines. The CO emission could be clearly seen, however, even in the spectrum corresponding to 8 gas kinetic collisions. The absorption by O_3 prevented its analysis and the poor overall signal precluded even an estimation of its population.

The relative populations of the observed vibrational levels of the HCl and OH produced in this reaction are presented as 3-dimensional plots in figures 36 and 37, respectively. The relative populations were determined from the spectra (as outlined in section II.A.2.) obtained at fourteen time delays after the laser fired. The values of the plotted populations are given in tables 4 and 5. Since the interferograms for all the time delays were collected concurrently, the populations were correlated, not only between the products at any one time delay but for each product from one time delay to the next.

In these figures, the observed vibrational levels are plotted on the x-axis, the average number of gas kinetic collisions after the laser fired (which represents the different time delays by the relation given in equation 5) at which the populations were determined is plotted on the y-axis, and the relative population is plotted on the z-axis. At each time

Figure 36: The time dependence of the relative vibrational populations of the HCl produced in the reaction $\text{O}^* + \text{CH}_3\text{Cl}$. The time axis is given as $\langle Z_{\text{gk}} \rangle$, the number of gas kinetic collisions of the HCl after the reaction was initiated.

Figure 37: The time dependence of the relative vibrational populations of the OH produced in the reaction $\text{O}^* + \text{CH}_3\text{Cl}$. The time axis is given as $\langle Z_{\text{gk}} \rangle$, the number of gas kinetic collisions of the HCl after the reaction was initiated.

Table 4: Values of the populations of each observed vibrational level and the total population of the HCl from the reaction $O^* + CH_3Cl$ for each time delay. The population for each vibrational level was obtained by summing the calculated populations of all the rotational levels with signal-to-noise greater than one belonging to that vibrational level. The errors in the vibrational populations were obtained by taking the square root of the sum of the squared errors in the rotational levels. The error in the total population was obtained by taking the square root of the sum of the squared errors in the vibrational levels.

Delay	$\langle Z_{gk} \rangle$	$v' = 1$	2	3	4	5	Sum
1	2.7	0.0838 ± 0.0139	0.0701 ± 0.0087	0.0422 ± 0.0069	0.0217 ± 0.0048	0.0102 ± 0.0035	0.2280 ± 0.0188
2	7.7	0.0808 ± 0.0143	0.0694 ± 0.0061	0.0468 ± 0.0076	0.0281 ± 0.0060	0.0060 ± 0.0022	0.2311 ± 0.0185
3	12.7	0.0883 ± 0.0125	0.0811 ± 0.0057	0.0530 ± 0.0058	0.0140 ± 0.0043	0.0069 ± 0.0028	0.2433 ± 0.0158
4	17.7	0.1003 ± 0.0061	0.0945 ± 0.0051	0.0434 ± 0.0040	0.0047 ± 0.0017		0.2429 ± 0.0091
5	22.7	0.1114 ± 0.0098	0.1033 ± 0.0051	0.0305 ± 0.0032			0.2452 ± 0.0115
6	27.7	0.1259 ± 0.0071	0.1030 ± 0.0048	0.0227 ± 0.0035			0.2516 ± 0.0092
7	32.7	0.1255 ± 0.0058	0.0892 ± 0.0045	0.0122 ± 0.0026			0.2269 ± 0.0078
8	37.7	0.1402 ± 0.0054	0.0807 ± 0.0039	0.0076 ± 0.0023			0.2285 ± 0.0070
9	42.7	0.1327 ± 0.0064	0.0776 ± 0.0040	0.0057 ± 0.0024			0.2161 ± 0.0080
10	47.7	0.1393 ± 0.0047	0.0617 ± 0.0032				0.2010 ± 0.0057
11	52.7	0.1366 ± 0.0042	0.0554 ± 0.0031				0.1920 ± 0.0052

Table 4 continued

Delay	$\langle Z_{gk} \rangle$	$v' = 1$	2	3	4	5	Sum
12	57.7	0.1250 ± 0.0048	0.0429 ± 0.0033				0.1679 ± 0.0058
13	62.6	0.1266 ± 0.0041	0.0380 ± 0.0021				0.1646 ± 0.0046
14	67.6	0.1003 ± 0.0039	0.0243 ± 0.0022				0.1246 ± 0.0045

Table 5: Values of the populations of each observed vibrational level and the total population of the OH from the reaction $\text{O}^* + \text{CH}_3\text{Cl}$ for each time delay. The population for each vibrational level was obtained by summing the calculated populations of all the rotational levels with signal-to-noise greater than one belonging to that vibrational level. The errors in the vibrational populations were obtained by taking the square root of the sum of the squared errors in the rotational levels. The error in the total population was obtained by taking the square root of the sum of the squared errors in the vibrational levels.

Delay	$\langle Z_{\text{gk}} \rangle$	$v' = 1$	2	3	4	5	Sum
1	3.0	undetected					
2	8.6	5.75 ± 1.48	3.87 ± 1.25	7.63 ± 0.75	7.08 ± 0.58		24.33 ± 2.16
3	14.1	6.10 ± 1.02	5.65 ± 0.84	8.92 ± 0.56	4.71 ± 0.78		25.37 ± 1.63
4	19.7	6.11 ± 1.48	6.79 ± 1.03	8.53 ± 0.75	3.46 ± 0.76		24.89 ± 2.09
5	25.2	8.08 ± 1.77	7.23 ± 1.12	8.47 ± 0.62	3.32 ± 0.61		27.10 ± 2.27
6	30.8	8.23 ± 2.00	6.72 ± 1.36	8.01 ± 0.63	2.50 ± 0.65		25.45 ± 2.58
7	36.3	7.04 ± 0.50	7.57 ± 0.89	7.84 ± 0.48	2.69 ± 0.49		25.14 ± 1.23
8	41.9	6.22 ± 1.97	6.58 ± 1.54	7.91 ± 0.58	1.81 ± 0.72		22.52 ± 2.66
9	47.4	4.31 ± 0.96	7.43 ± 1.16	7.07 ± 0.65	1.63 ± 0.73		20.44 ± 1.79
10	53.0	7.89 ± 1.78	7.39 ± 1.16	6.78 ± 0.48			22.06 ± 2.18
11	58.6	6.11 ± 2.15	6.95 ± 0.91	7.68 ± 0.42			20.74 ± 2.37

Table 5 continued

Delay	$\langle Z_{gk} \rangle$	$\nu' = 1$	2	3	4	5	Sum
12	64.1	6.32 ± 2.03	7.17 ± 0.94	6.15 ± 0.66			19.64 ± 2.33
13	69.7	6.32 ± 1.17	8.22 ± 0.59	5.04 ± 0.39			19.69 ± 1.36
14	75.2	5.66 ± 0.79	8.31 ± 0.32	4.65 ± 0.41			18.62 ± 0.95

delay (or number of gas kinetic collisions as plotted in the figures), the relative population of each vibrational level having lines with signal to noise greater than one was determined. These populations are represented on the plot as a series of points connected by dotted lines. The first point in each time delay set is for vibrational level 1, the second point for vibrational level 2, and so on. To aid in identifying those points in a set belonging to one time delay, each set of points is marked with a different symbol: the first set of populations (time delay 1) by diamonds ($\diamond$), the second set of populations (time delay 2) by inverted triangles (∇), and so on. The first set of points (figure 36) show the HCl population at 2.7 gas kinetic collisions. These are connected to the grid in the x-y plane by thin solid lines. The positions on the x-y grid at which each thin solid line terminates indicates the v' -levels and $\langle Z_{gk} \rangle$ of the first set of points. The time evolution of each vibrational level is shown by the thick lines connecting the different symbols for the different time delays: solid for $v' = 1$ and 4, dashed for $v' = 2$ and 5, and chain-dashed for $v' = 3$ and 6. The points were fitted by least-squares analysis, with the weighting factor for each vibrational level equal to approximately three quarters of the average error in the populations for that v' -level. Only those v' -levels with more than four values were handled this way due to the fitting routine, those with four or less values were simply connected (dot-to-dot) by lines. The splining produced reasonably smooth curves, where the deviation of the experimental points from the calculated line was representative of their error. These curves were projected onto the grid in the y-z plane as thin lines (with the same convention to identify the v' -levels as was used in drawing the thick lines) to assist in determining the population of any v' -level at any $\langle Z_{gk} \rangle$ value. Each curve is labelled at its beginning by the v' number of the level to which it corresponds.

The relative populations of the vibrational levels $v' = 1$ to $v' = 5$ for HCl obtained at 2.7 average gas kinetic collisions were 0.084 ± 0.014 , 0.070 ± 0.009 , 0.042 ± 0.007 , 0.022 ± 0.005 , and 0.010 ± 0.004 . These values were not normalized or scaled but were the values as calculated by the population analysis program. They do not represent absolute intensities since the detection system was not calibrated. The values given above were obtained at the earliest observation time used in this study, *ie.* the first time delay after the reaction was initiated, corresponding to 2.7 gas kinetic collisions (of which, on the average, one was required for reaction). Each of the observed vibrational levels had a fully resolved rotational structure as evident in figure 34 and appendix A.3. At this time delay, rotational levels were analyzable (had signal to noise greater than one) up to $J' = 18$ in the first three vibrational levels and up to $J' = 13$ and 8 for v' -levels 4 and 5 respectively. These initial rotational distributions were essentially flat with only a slight indication of a Boltzmann distribution due to rotational relaxation in the lower v' -levels. By the third time delay ($\langle Z_{\text{gk}} \rangle = 12.7$) the rotational distributions were essentially relaxed with most of the population in a Boltzmann distribution at a rotational temperature of approximately 300 K. The obvious emergence of the relaxed Boltzmann distribution leads to the expectation that the observed distribution did indeed closely approximate the nascent distribution due to reaction with minimal deviation due to rotational relaxation. In addition, the slow emergence of the Boltzmann distribution argues for very high rotational excitation of the HCl from this reaction; rapid (greater than gas kinetic) rotational relaxation (by thermal HCl) occurs for the lower J-levels, with generally decreasing rates as the initial J-level increases⁹⁵. If a similar trend in rates occurs for deactivation by O_3 and CH_3Cl , complete relaxation would be slow (requiring many collisions) only if the initial population was extensively in the higher J-levels.

When the populations obtained in this study were combined with that of Lin⁶⁵, the relative populations of the first six vibrational levels of HCl were 0.14, 0.084, 0.070, 0.042, 0.022, and 0.010 scaled to the measured population of $v' = 1$. This distribution (the earliest determined in this study) is plotted in figure 38. As stated in the previous sub-section, the value from Lin may have been influenced by vibrational relaxation. As a result, the distribution presented in figure 38 can have three interpretations. If the value for $v' = 0$ was actually much lower than depicted, then the vibrational distribution was substantially more excited (or possibly inverted) than what would be statistically expected (as from a long-lived collision complex). If the value for $v' = 0$ calculated from the results of Lin was approximately correct, then the distribution was slightly more excited than a statistically expected one and the small inflection at $v' = 2$ may have no significance but merely be due to the errors in the calculated values. Finally, if the proper value for $v' = 0$ was much higher than the calculated value, then the distribution would more closely approximate a statistical one, and the inflection at $v' = 2$ would be significant.

The time evolution of the individual vibrational levels is given in figure 36 by the heavy lines connecting the varying symbols for each v' -level and by their projection on the backplane. The population in $v' = 5$ decreased monotonically within its error (the line drawn for this level could not be splined and simply connected the individual values). All other levels exhibited an increase in population followed by a more rapid decrease. A qualitative analysis of the vibrational relaxation, similar to that used in evaluating the results of Lin⁶⁵ in the previous sub-section, can be applied here. With an $O_3:CH_3Cl$ partial pressure ratio of 1:1, the rate^{91,96} per gas kinetic collision for vibrational deactivation of levels $v' = 1, 2, 3, 4$, and 5 are 0.0171, 0.029, 0.087, 0.31, and 0.51. These values were obtained by averaging the rates for deactivation by O_3 and CH_3Cl and

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Figure 38: The initial relative vibrational populations of the HCl (○) and OH (□) produced in the reaction $\text{O}^* + \text{CH}_3\text{Cl}$. The $v' = 0$ value is taken from Lin⁶⁵ and scaled to the $v' = 1$ value obtained in the present study. The OH populations are scaled by a factor of 0.01. The lines connect the points corresponding to each molecule and do not represent a functional fit.

then dividing this value by the rigid sphere rate for a gas kinetic collision of HCl in 1 atmosphere of O₃ and CH₃Cl with equal partial pressures ($1.834 \times 10^{10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) to give $\bar{k}_g$, the deactivation per gas kinetic collision. The value for deactivation of $v' = 1$ by CH₃Cl was determined by extrapolation using the values for $v' = 2$ to 7 and all values for deactivation by O₃ were taken to be equal to those for CO. This value of $\bar{k}_g$ gives an approximation to the probability for deactivation by one quantum from level v' at the time t , $P_{v'}(t)$:

$$\begin{aligned} P_{v'}(t) &= k_g(v'-1 \leftarrow v')_{\text{O}_3} * \langle Z_{\text{gk}} \rangle_{\text{O}_3}(t) + k_g(v'-1 \leftarrow v')_{\text{CH}_3\text{Cl}} * \langle Z_{\text{gk}} \rangle_{\text{CH}_3\text{Cl}}(t) \\ &\approx (\langle Z_{\text{gk}} \rangle_{\text{O}_3}(t) + \langle Z_{\text{gk}} \rangle_{\text{CH}_3\text{Cl}}(t)) * (k_g(v'-1 \leftarrow v')_{\text{O}_3} + k_g(v'-1 \leftarrow v')_{\text{CH}_3\text{Cl}}) / 2 \\ &\approx z(t) * \bar{k}_g \end{aligned} \quad 6$$

where $k_g(v'-1 \leftarrow v')_{\text{O}_3}$ is the gas kinetic rate for deactivation of v' by O₃ and, similarly, $k_g(v'-1 \leftarrow v')_{\text{CH}_3\text{Cl}}$ by CH₃Cl. $\langle Z_{\text{gk}} \rangle_{\text{O}_3}(t)$ and $\langle Z_{\text{gk}} \rangle_{\text{CH}_3\text{Cl}}(t)$ are the number of gas kinetic collisions of the *product* with O₃ and CH₃Cl respectively at the time t which, when added, give the quantity $z(t)$, the number of deactivating collisions. The number of deactivating collisions was equal to $(\langle Z_{\text{gk}} \rangle(t) - 1)$ where $\langle Z_{\text{gk}} \rangle(t)$ is defined in equation 5 ($\langle Z_{\text{gk}} \rangle(t)$ is the quantity used throughout this section to denote the time (after initiation of reaction) at which observations were made). This assumes that the HCl was produced in the first gas kinetic collision (thus requiring the subtraction of 1) which is reasonably valid since the reaction rate is nearly gas kinetic. The relationship in equation 6 is a valid approximation as long as either the two deactivation rates, k_g , or the two collisions, $\langle Z_{\text{gk}} \rangle_M$, are nearly equal. For equal partial pressures of O₃ and CH₃Cl, the latter qualifier is valid. Using the deactivation values listed above, the probabilities of deactivation by one quantum of energy prior to the first observation time for levels 1 to 5 were 0.029, 0.050, 0.15, 0.53, and 0.87. From these values, $v' = 5$ had undergone

substantial relaxation, while $v' = 4$ was significantly relaxed by even the first time delay. In addition, since the probability for deactivation increases with v' , each lower level could form a blockage since, depending on the relative populations, there could be more molecules relaxing into a level than out of it until the population in the upper level was sufficiently small. This phenomena could be responsible for the increase and subsequent decrease in the populations of levels 1 to 4, although this explanation was not entirely satisfactory. The shapes of the time evolution curves (especially for $v' = 1$ and 2) were more gradual than expected from the deactivation probabilities listed above.

The extent of total relaxation evidenced by the emergence of the Boltzmann rotational distribution (which was relatively slow) and that indicated from the argument above for vibrational relaxation which indicated that the higher vibrational levels were notably relaxed even by the first time delay did not agree well. The actual degree of total relaxation was probably somewhere between the two estimates, but closer to the latter. Since rotational relaxation is not as rapid for higher J states, whereas vibrational relaxation is faster for higher v states, the higher vibrational levels would have relaxed vibrationally before they were fully relaxed rotationally. As a result, the vibrational distribution listed above was expected to be a lower limit to the nascent distribution, particularly for the higher vibrational levels.

The emission from the OH produced in reaction (2h) was below the detection limit in the spectrum for the first time delay taken after the laser fired. It was, however, apparent in the spectrum for the second time delay which represented 8.6 gas kinetic collisions for the OH with the ambient gas. OH emission was observed at this time delay for $v' = 1$ to 4 which was the maximum vibrational level energetically allowed for this reaction. The calculated relative populations for vibrational levels $v' = 1$ to 4 were 5.8 ± 1.5 ,

3.9 ± 1.3 , 7.6 ± 0.8 , and 7.1 ± 0.6 . This distribution, scaled by a factor of 0.01, is plotted in figure 38. Due to the large errors in the populations, it was difficult to determine if the bimodal behaviour of this distribution was physically significant.

The OH rotational populations of each vibrational level at this time delay consisted only of a Boltzmann distribution at approximately 300 K. If higher rotational levels were populated, they may not have been observed due to insufficient intensity. The emergence of the low J-level Boltzmann distribution may have been due to rotational relaxation and could indicate that higher rotational levels had been populated and subsequently deactivated. That the lower rotational states were observable after relaxation whereas the higher states were not was possible only if the higher states had very low populations since OH A-factors increase with rotational level for all J-states observable in this experiment⁸². The only other explanation for the appearance of only low rotational states in a Boltzmann distribution was that this was the nascent rotational distribution due to reaction - with the large exothermicity from this reaction and the expected insertion dynamics, this was not expected to be a plausible explanation. Whether the rotationally relaxed Boltzmann distribution represented the entire rotational population reliably could not be determined from these results. This indicated that the error bars on the initial vibrational distribution should be larger than what was calculated from the population analysis program. The lower the vibrational level, the larger the number of energetically accessible rotational levels, therefore, a larger fraction of the total population in the lower v' -levels resides in the high rotational levels. If the Boltzmann population was entirely due to relaxation of the mid-J population and the high-J population was not relaxed sufficiently to contribute to it, then the lower v' -levels would have anomalously small values.

The time profiles of the individual vibrational levels are given in figure 37 as thick lines connecting the various symbols for each level and by their projection on the backplane. As explained previously, these lines were calculated by a least squares fit to the data and the deviation of the points from the lines was indicative of the errors in the values. The increased error in the lower vibrational levels was due to the method used to correct the spectra for system sensitivity. In the uncorrected spectra, the noise remained basically constant over the entire spectral range. When the spectra were corrected for the system response, the height of the noise was increased along with the spectral lines. As a result, the noise in the spectral region around $v' = 1$ increased as compared to that around $v' = 4$. This resulted in smaller errors for the higher vibrational levels than for the lower ones. The population in $v' = 4$ decreased almost monotonically. The slight increase around 40 gas kinetic collisions was not necessarily significant, but could have been an artifact of the weighting parameter used to draw the splined fit of that level. Levels 1 and 3 increased slightly and then slowly decreased. The population for $v' = 2$ increased during the entire time of observation. These results cannot be made compatible with expected vibrational relaxation.

The vibrational relaxation of free radicals (such as OH) have not received as much attention as stable molecules (such as the halogen hydrides) and the mechanisms responsible for relaxation are still not fully understood. There does appear to be a class of relaxers for OH, however, which does follow a relationship between relaxation rate and energy defect^{97,98} similar to that found for relaxation of the hydrogen halides. The lines for non-polar molecules on the Lambert-Slater plots (rate constant versus energy defect) for vibrational levels 1 and 2 of OH and HCl are almost coincident⁹⁷, indicating that a similar relaxation mechanism appears to be operative in the two molecules. In the relaxation of HCl, the halogenated methanes (moderately polar molecules) do not follow

the same trend as the non-polar molecules, and have substantially larger rates⁹⁹ than CH₄ (which has a comparable energy defect) for all observed levels: CH₃Cl has rates ranging from 2.5 to 18 times those for CH₄ depending on vibrational level. A similar trend is observed in the relaxation of OH by NH₃, a highly polar molecule, where the observed rate is 60 times larger than expected from an energy defect plot for non-polar molecules⁹⁸. In addition, for both polar and non-polar molecules, the relaxation rate increases with increasing vibrational level. Even though relaxation of OH by O₃ has not been measured for the low vibrational levels observed in this study, it should fall into the same pattern as the other non-polar oxides⁹⁸ and have rates similar to those of N₂O which has an energy defect almost equal to that of O₃ (if relaxation is by the combination bands $2\nu_1$ and $\nu_1 + \nu_3$ of O₃). This rate has been measured⁹⁸ to be $4.6 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for relaxation out of $\nu' = 2$, and the rate for $\nu' = 1$ can be estimated⁹⁷ as $3 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The relaxation rates of $\nu' = 1$ and 2 have been measured⁹⁷ for CH₄ to be 5.3 and $12.5 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ respectively, and the rates for the polar molecule CH₃Cl are expected to be on the order of 10 times these values. Using these values for the relaxation rates and a gas kinetic rate of $2.04 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for OH, then the probabilities for losing one quantum of vibrational energy by the second time delay (8.6 gas kinetic collisions) for these two levels as given in equation 6 are 0.11 and 0.28. Despite the actual values of these probabilities, their relative values (relaxation from $\nu' = 1$ is slower than from 2 due to the larger energy defect) ensures that the population in vibrational level 1 will relax slower than that of level 2. As a result, the population in $\nu' = 1$ must increase as long as the population in $\nu' = 2$ is greater. After approximately 30 gas kinetic collisions, the ratio N_2/N_1 was greater than 1, yet the population in $\nu' = 1$ continued to decrease. With normal vibrational relaxation (as expected for the relaxation of OH by O₃ and CH₃Cl) this is physically impossible. One

explanation for this non-physical behaviour was the extreme scatter in the points, especially for the two lower vibrational levels. Despite the uncertainty in the time profiles of these levels, it was apparent that the three lower vibrational levels did not relax at a rate comparable to what would be expected from the values given above ($\bar{k}_g = 0.013$ and 0.032 for $v' = 1$ and 2 respectively), particularly since the deactivation probability was expected to increase for $v' = 3$. This level should have shown substantial relaxation by the last data point (75.2 gas kinetic collisions) similar to that of $v' = 4$.

II.B.2. $O(^1D_g) + CH_3F$

II.B.2.a. Overview: $O(^1D_g) + CH_3F$

The pertinent channels for the reaction of O^* with CH_3F are:

The only products from this reaction which had rovibrational bands situated in the range of the detector and had sufficient intensity to be observable were HF, CO and OH, occurring in reactions (3a) to (3e) and (3h). Reaction (3b), even though it has the same products as reaction (3a), must be considered as a separate channel as discussed in section II.B.1.a. Again, reactions (3c) to (3e) are expected to be predominantly the result of predissociation along the $CH_2O(A^1A'')$ surface. Reactions (3f,g) and (3i,j,k) were not observed but pertain to the discussion below. Reaction (3i), abstraction of the halogen

atom, is endothermic and is not available for reaction with the initial reagent energy (approximately 8 kJ/mole) used in this study.

The estimated deactivation rate⁸⁶, calculated from equation 3 is $1.0 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The calculated rate is in adequate agreement with the experimental rate⁵⁹ $1.38 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, where 25% of the O^* deactivation rate was determined to be quenching (reaction (3k)) and 75% reaction.

The reactive branching ratios (reactions (3a) to (3j)) have not been determined experimentally. From the allowed reactions and equation 3, the C-H bonds contribute to quenching and to the formation of OH, HF, H_2 , and H (again, the last two products will be considered to be minor channels, as discussed in the previous reaction, and will be ignored). The C-F bond contributes only to the formation of HF and F. The latter product channel is considered insignificant as discussed in the previous reaction for the Cl product channel. CH_4 does not quench⁵⁹ O^* and C-H bonds in CH_3F should be just as ineffective at quenching, requiring the C-F bond to contribute entirely to quenching (25% of the deactivation rate). The C-H bond must contribute an equivalent amount to reactions (3a) to (3e) as does the C-F bond since there is one H and one F in HF. Therefore, the rate constant for reactions (3a) to (3e) (from equation 3 and the above arguments) would be $0.045 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and that leaves $0.938 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for the rate of reaction (3h) (with $0.023 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ of the C-H bond contribution given to formation of HF). Based on these rates, the branching ratio for this reaction is $[\text{OH}]/[\text{HF}] = 20.8$. In equation 3, the value 0.03 for the C-F bond contribution was determined by Davidson *et al.*⁸⁶ primarily from a single experimental value (the deactivation rate of CF_4). All other molecules containing F atoms used in their determination had rates dominated by H or Cl atoms, according to

the bond additivity scheme and the bond contributions expressed in equation 3. The branching ratio for reactions (3a) to (3e) and (3h) is very sensitive to the contribution to reaction from the C-F bond. For example, if the contribution from a C-F bond was $0.01 * 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ rather than $0.03 * 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, the branching ratio would increase to 63.5. Determination of this ratio would be a sensitive test of the contribution of the C-F bond if the bond additivity expressed in equation 3 is valid.

The dynamics of this reaction has been investigated by Burks and Lin⁶⁷ by observing the appearance time of the HF laser emission following reaction. The measured relative population distribution in the first four v' -levels was 1.0, 0.88 ± 0.02 , 0.64 ± 0.06 , and ≤ 0.41 . This distribution was 'hotter' (the populations of the vibrational levels did not decrease as rapidly with v' -level as expected) than any of three different calculated statistical distributions it was compared to, indicating that the HF could not come from a long-lived intermediate that had sufficient time to statistically distribute the reaction exoergicity. In addition, they found that the HF had high rotational excitation indicating that the lighter H atom had to leave the excited complex first. They concluded that the HF was formed as a result of a rapid decomposition of the insertion intermediate CH_2FOH .

An analysis of the experimental conditions indicates that this distribution should be closer to the nascent vibrational distribution than was found for the HCl from reaction with CH_3Cl as discussed for the previous reaction. The $\text{O}_3/\text{CH}_3\text{F}/\text{SF}_6$ partial pressures used⁶⁷ were 1/2/140 at a total pressure of 20 Torr. The substantially larger partial pressure of SF_6 as opposed to that used in Lin's measurement of the HCl populations⁶⁵ from reaction with CH_3Cl resulted in insignificant vibrational relaxation of the HF prior

to the onset of lasing. Both SF_6 and CO (used to estimate the rates for O_3) are known⁹⁹ to be less efficient at relaxing HF than HCl . There has been no determination of the relaxation rates of HF by CH_3F , although it should be less efficient than CH_3Cl relaxing HCl due to the larger spacing of the rovibrational levels in HF. The combined effect of slow vibrational relaxation and the increased partial pressure of SF_6 (which has the smallest rate of all three relaxers) resulted in very little vibrational relaxation.

II.B.2.b. Experimental Results: $\text{O}(^1\text{D}_g) + \text{CH}_3\text{F}$

The partial pressures of O_3 and CH_3F were 10 mTorr each. As in the previous reaction, interferograms were collected at a total of fifteen time delays simultaneously. The populations for different products observed at any time delay and for a single product for successive time delays were, therefore, correlated. The 'zeroth' time delay was at 17 μs prior to the photolysis pulse and showed no discernible emission, confirming that the reaction chamber was adequately cleared of products resulting from the previous laser pulse. The first time delay was approximately 21 μs after reaction was initiated and measurements were taken at about every 38.5 μs thereafter for a total of 14 time delays.

The earliest time at which HF emission was measured was 21 μs , corresponding to an average of 2.6 gas kinetic collisions by the time of observation. The earliest time at which OH emission was measured was 136.5 μs , corresponding to an average of 19.7 gas kinetic collisions prior to observation. Sample spectra obtained for this reaction are given in figures 39 and 40. The spectra in figure 39 were taken at 3 (bottom), 12, 36 and 65 (top) average gas kinetic collisions of the HF. Identification of the individual lines is facilitated by the template at the top of the figure. Only the P branches for the first five v' levels are indicated with a maximum J of 21. R branch lines were not identified in the template, even though they were present in the spectra, as they had substantially lower

Figure 39: Sample HF emission spectra from the reaction $O^* + CH_3F$ for approximately 3 (bottom), 12, 36, and 65 (top) gas kinetic collisions of the HF with the ambient gas in the reaction chamber. The templates at the top of the figure identifies the rovibrational lines of HF.

Figure 40: Sample OH emission spectra from the reaction $\text{O}^* + \text{CH}_3\text{F}$ for approximately 17 (bottom), 36, 55, and 65 (top) gas kinetic collisions of the OH with the ambient gas in the reaction chamber. The templates at the top of the figure identifies the rovibrational lines of OH.

intensity than the comparable line in the P branch due to their smaller A-factors. The slight undulation in the baseline of the second spectrum (for 12 average gas kinetic collisions) was due to a transient in one of the interferograms and does not represent a physically significant feature. In addition, it did not interfere with the analysis since the heights of the spectral lines were measured from their local baselines. The high rotational excitation of the initial HF is readily seen in the first spectrum (at 3 average gas kinetic collisions); the highest rotational level that was identified was $^2P_{26}$. The rotational relaxation of the HF was apparent from the large reduction in lines from one spectrum to the next.

The four spectra in figure 40 depict the OH emission observed as a result of reaction. They are for 17 (bottom), 36, 55, and 65 (top) average gas kinetic collisions of the OH. The line positions of the P and Q branches for the first four v' -levels are indicated at the top, in similar fashion as described in the previous section for figure 34. The first spectrum ($\langle Z_{gk} \rangle = 17$) is severely overlapped with HF lines which, with the poor signal to noise, made analysis very difficult. The first three time delays showed no apparent OH emission, even for the few OH lines that were not overlapped by HF. This point will be discussed later.

There was no convincing evidence for the formation of CO found in any of the spectra from this reaction, although a few CO lines could be tentatively identified in some of the spectra. This was not conclusive proof that CO was not formed since interferograms were coadded only until adequate signal to noise (around 20 to 1) was obtained for the HF lines. Since the A factors for CO are approximately a factor of 5 smaller than those for HF, the CO emission may have been too weak to be detectable above the noise.

Detection of CO was also hindered by O₃ absorption as discussed for the previous reaction.

The relative populations were determined from the spectra (as outlined in section II.A.2.) at each of the fourteen time delays following the photolysis laser pulse. The populations of the observed vibrational levels of the HF and OH produced in this reaction are presented as 3-dimensional plots in figures 41 and 42 respectively. The description of these plots is given in section II.B.1.b. for the analogous plots from the previous reaction. The values of the populations plotted in these figures are given in tables 6 and 7 respectively.

The relative populations of the vibrational levels $v' = 1$ to 5 for the HF produced in reactions (3a) to (3e) were 0.0223 ± 0.0016 , 0.0159 ± 0.0015 , 0.0102 ± 0.0007 , 0.0056 ± 0.0005 , and 0.0027 ± 0.0005 . Again, these values were those given by the population analysis program without normalization or scaling. These values were obtained at the earliest observation time used in this study (21 μ s after the laser fired) and corresponded to 2.6 gas kinetic collisions (of which at least one collision was required for reaction). Each of the observed vibrational levels had a resolved rotational structure, as evident in figure 39. The maximum analyzable rotational levels at this time delay for vibrational levels 1 to 5 were $J' = 25, 26, 23, 22$, and 16 respectively. The rotational distributions after 2.6 gas kinetic collisions were essentially flat with only a slight indication of a relaxed Boltzmann distribution evident for the lower three vibrational levels. Complete rotational relaxation (where only a Boltzmann distribution at approximately 300 K was detectable) did not occur until the seventh or eighth time delay, after approximately 35 gas kinetic collisions, at which time only $v' = 1$ and 2 remained detectable. The obvious emergence with time of the relaxed Boltzmann rotational

Figure 41: The time dependence of the relative vibrational populations of the HF produced in the reaction $\text{O} + \text{CH}_3\text{F}$. The time axis is given as $\langle Z_{gk} \rangle$, the number of gas kinetic collisions of the HF after the reaction was initiated.

Figure 42: The time dependence of the relative vibrational populations of the OH produced in the reaction $\text{O}^* + \text{CH}_3\text{F}$. The time axis is given as $\langle Z_{\text{gk}} \rangle$, the number of gas kinetic collisions of the OH after the reaction was initiated.

Table 6: Values of the populations of each observed vibrational level and the total population of the HF^+ from the reaction $\text{O}^+ + \text{CH}_3\text{F}$ for each time delay. The population for each vibrational level was obtained by summing the calculated populations of all the rotational levels with signal-to-noise greater than one belonging to that vibrational level. The errors in the vibrational populations were obtained by taking the square root of the sum of the squared errors in the rotational levels. The error in the total population was obtained by taking the square root of the sum of the squared errors in the vibrational levels.

Delay	$\langle Z_{gk} \rangle$	$v' = 1$	2	3	4	5	Sum
1	2.6	0.0223 ± 0.0016	0.0159 ± 0.0015	0.0102 ± 0.0007	0.0056 ± 0.0005	0.0027 ± 0.0005	0.0567 ± 0.0024
2	7.5	0.0233 ± 0.0013	0.0163 ± 0.0007	0.0072 ± 0.0005	0.0027 ± 0.0003		0.0495 ± 0.0016
3	12.3	0.0291 ± 0.0015	0.0170 ± 0.0008	0.0048 ± 0.0004			0.0509 ± 0.0017
4	17.1	0.0330 ± 0.0012	0.0162 ± 0.0006	0.0029 ± 0.0002			0.0512 ± 0.0014
5	22.0	0.0318 ± 0.0011	0.0111 ± 0.0006	0.0008 ± 0.0002			0.0436 ± 0.0013
6	26.8	0.0328 ± 0.0016	0.0075 ± 0.0006	0.0004 ± 0.0004			0.0407 ± 0.0017
7	31.6	0.0335 ± 0.0012	0.0061 ± 0.0003	0.0006 ± 0.0001			0.0401 ± 0.0013
8	36.5	0.0311 ± 0.0011	0.0042 ± 0.0006				0.0353 ± 0.0013
9	41.3	0.0283 ± 0.0012	0.0033 ± 0.0005				0.0316 ± 0.0013
10	46.2	0.0214 ± 0.0007	0.0016 ± 0.0002				0.0230 ± 0.0007
11	51.0	0.0192 ± 0.0004	0.0013 ± 0.0001				0.0205 ± 0.0005

Table 6 continued

Delay	$\langle Z_{gk} \rangle$	$v' = 1$	2	3	4	5	Sum
12	55.8	0.0189 ± 0.0006	0.0012 ± 0.0001				0.0201 ± 0.0006
13	60.7	0.0179 ± 0.0007	0.0011 ± 0.0002				0.0190 ± 0.0008
14	65.5	0.0155 ± 0.0006	0.0009 ± 0.0001				0.0164 ± 0.0006

Table 7: Values of the populations of each observed vibrational level and the total population of the OH from the reaction $O^+ + CH_3F$ for each time delay. The population for each vibrational level was obtained by summing the calculated populations of all the rotational levels with signal-to-noise greater than one belonging to that vibrational level. The errors in the vibrational populations were obtained by taking the square root of the sum of the squared errors in the rotational levels. The error in the total population was obtained by taking the square root of the sum of the squared errors in the vibrational levels.

Delay	$\langle Z_{gk} \rangle$	$v' = 1$	2	3	4	5	Sum
1	3.0	undetected					
2	8.6	undetected					
3	14.1	undetected					
4	19.7	0.73 ± 0.28	0.75 ± 0.14	0.88 ± 0.24			2.36 ± 0.40
5	25.2	0.87 ± 0.44	0.58 ± 0.29	1.09 ± 0.27			2.54 ± 0.59
6	30.8	0.99 ± 0.38	1.06 ± 0.25	0.84 ± 0.22			2.89 ± 0.51
7	36.3	0.72 ± 0.37	0.82 ± 0.26	0.75 ± 0.20			2.30 ± 0.50
8	41.9	1.12 ± 0.23	0.81 ± 0.23	0.68 ± 0.19			2.61 ± 0.38
9	47.4	1.06 ± 0.25	1.03 ± 0.16	0.79 ± 0.13			2.88 ± 0.32
10	53.0	0.72 ± 0.27	0.65 ± 0.27	0.47 ± 0.16			1.85 ± 0.35
11	58.5	1.21 ± 0.13	0.92 ± 0.21	0.38 ± 0.18			2.51 ± 0.31

Table 7 continued

Delay	$\langle Z_{gk} \rangle$	$\nu' = 1$	2	3	4	5	Sum
12	64.0	0.91 ± 0.18	0.92 ± 0.16	0.52 ± 0.08			2.36 ± 0.25
13	69.6	1.00 ± 0.17	1.06 ± 0.10				2.06 ± 0.20
14	75.1	0.79 ± 0.23	0.85 ± 0.17				1.64 ± 0.28

distribution indicated that very little rotational relaxation had occurred prior to the first time delay. It also indicated that the original HF from this reaction had very high rotational excitation.

When the populations obtained in this study were combined with the N_1/N_0 ratio of Burks and Lin⁶⁷, the relative populations of the first six vibrational levels of HF were 0.0153, 0.0223, 0.0159, 0.0102, 0.0056, and 0.0027 scaled to the population of $v' = 1$ obtained in this study. This distribution (the earliest determined in this study) multiplied by a factor of 100, along with the distribution for the first four vibrational levels from Burks and Lin⁶⁷ (scaled to the population of $v' = 1$) are plotted in figure 43. The agreement between the two distributions was very good. Since the initial distribution from this study was basically unrelaxed, the supposition that Burks and Lin's distribution was not affected by relaxation was supported. As in the previous reaction, the distribution when combined with Burks and Lin's value for $v' = 0$ displayed a slight inflection, occurring at $v' = 1$.

The time evolution of the individual vibrational levels is given in figure 41 by the heavy lines connecting the various symbols for each v' -level and by their projection on the backplane. The populations in $v' = 3, 4$, and 5 decreased monotonically from their initial values until they were below the detection limit of this experiment. The population of $v' = 2$ increased slightly, reached a peak after approximately 25 gas kinetic collisions and then gradually decreased. This behaviour can be explained if the relaxation rates and relative populations of this and higher levels caused a buildup at this level, that is, the population relaxing into this level exceed that relaxing out of it. The population in $v' = 1$ increased from its initial value, peaked around 32 gas kinetic collisions and then gradually decreased. Again, this feature could be due to a relaxation buildup at this level.

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Figure 43: The initial relative vibrational populations of the HF (□) and OH (■) produced in the reaction $\text{O}^* + \text{CH}_3\text{F}$. The HF results of Burks and Lin⁶⁷ scaled to the $v' = 1$ value obtained in the present study is also presented (Δ). The HF populations are scaled by a factor of 100. The lines connect the points corresponding to each molecule and do not represent a functional fit.

The best estimate of the deactivation probabilities for levels 1 and 2 under the conditions of this experiment were 0.0016 and 0.0046 respectively. The rather large ratio between these two rates and their relatively small values would produce vibrational relaxation similar to that seen for these two levels.

The first analyzable distribution for the OH observed from this reaction occurred in the spectrum taken at the fourth time delay. This corresponded to 19.7 gas kinetic collisions of the OH with the ambient gas. The relative populations for vibrational levels $v' = 1$ to 3 at this time delay were 0.73 ± 0.28 , 0.75 ± 0.14 , and 0.88 ± 0.24 . This distribution, scaled by a factor of 10 is plotted in figure 43. The exceedingly large errors in these values precluded any statement being made about the apparent increase in population with v' for these three levels. It was evident, however, that this distribution indicated greater than statistical vibrational excitation. No emission from levels $v' = 4$ or 5 was observed, although these levels were energetically accessible.

It was not possible to determine from these results whether OH was undetected at earlier time delays due to insufficient intensity or from other causes. Only the lowest rotational levels corresponding to a Boltzmann distribution were present at any time delay where OH was detected. As in the case for OH from the reaction of O^* with CH_3Cl , this was indicative of relaxation from higher rotational levels. If the OH population was distributed over a large number of rovibrational states, it would be undetectable due to the relatively small A-factors for OH compared to those for HF. As a result, substantial rotational relaxation would have to occur before sufficient population had accumulated in the lower rotational levels to make detection possible. Even though this was not conclusive, high rotational excitation could explain the absence of OH emission in the first three spectra.

The time evolution of the OH vibrational levels is given in figure 42 by the heavy lines connecting the individual symbols for each level and from their projection on the backplane. The data used to calculate these lines had large errors, as indicated by the large displacement of the points from the lines (the lines represent a least squares fit weighted by the errors of the points). Despite the large errors in individual values, definite trends were indicated. The population in $v' = 3$ decreased monotonically from its first value which could be the result of slow vibrational relaxation. The populations in $v' = 1$ and 2 gradually increased for most of the observation time (only $v' = 1$ showed an actual decrease). Even though the actual profiles for these levels were unknown due to the large errors, a definite persistence of emission in levels $v' = 1$ and 2 was indicated. As with the OH observed in the previous reaction, this behaviour was incompatible with the expected rate of vibrational relaxation for these levels under the conditions of the experiment.

II.B.3. $O(^1D_g) + CHClF_2$

II.B.3.a. Overview: $O(^1D_g) + CHClF_2$

The relevant reactive channels for the reaction of O^* with $CHClF_2$ are:

		ΔH_0^0 (kJ/mole)	
$O^* + CHClF_2 \rightarrow$	$HF + CCIFO(X^1A_1)$	-658	(4a)
	$HF + CCIFO(A^1A'')$	-220	(4b)
	$HF + CO + ClF$	-388	(4c)
	$HF + CO + Cl\cdot + F\cdot$	-141	(4d)
	$HF + \cdot CClO + F\cdot$	-168	(4e)
	$HF + \cdot CFO + Cl\cdot$	-279	(4f)
	$HCl + CF_2O(X^1A_1)$	-682	(4g)
	$HCl + CF_2O(A^1A'')$	-214	(4h)
	$H\cdot + CCIF_2O\cdot$	-182	(4i)
	$\cdot OH + \cdot CF_2Cl$	-185	(4j)
	$FO\cdot + \cdot CHClF$	+73	(4k)
	$ClO\cdot + \cdot CHF_2$	-140	(4l)
	$FCl + CHFO$	-385	(4m)
	$F_2 + CHClO$	-105	(4n)
	$F\cdot + CHClFO\cdot$	-83	(4o)
	$Cl\cdot + CHF_2O\cdot$	-195	(4p)
	$\cdot CF_2 + HOCl$	-214	(4q)
	$\cdot CF_2 + \cdot OH + Cl\cdot$	+21	(4r)
	$\cdot CF_2 + HCl + \cdot O(^3P)$	+17	(4s)
	$O(^3P) + CHClF_2$	-190	(4t)

Of all the possible products listed above, only HF, HCl, OH, and CO had rovibrational bands within the range of the detector and were expected to have sufficient intensity to be observable, depending on the branching ratios into the different reactions. Even though many of the channels listed for this reaction were unobservable, they have been included due to their relevance to discussions below. As in the previous reactions, several channels could be connected to one reaction mode, *ie.* reactions (4a) to (4f) represent the primary product HF, resulting from molecular elimination, where the polyatomic product in this reaction channel (CCIFO) has two accessible electronic states and several predissociation modes of the excited electronic state. Similarly, reactions (4g,h) involve the primary production of HCl: no predissociation modes of the polyatomic fragment are included since $\text{CF}_2\text{O}(\text{A}^1\text{A}^{\prime\prime})$ is stable. Reaction (4i), H-atom substitution, is the result of insertion and should be a minor channel compared to production of HF or HCl as discussed in the previous reactions. The production of OH, (4j), can occur by either abstraction or insertion. Reactions (4k,l) are the halogen abstractions, of which fluorine abstraction is endothermic. Reactions (4m,n,o,p) involve the elimination of halogens and are not expected to contribute significantly to the reaction rate and will be ignored: as with the previous reactions, the interaction of O^* with a halogen bond is expected to proceed entirely by abstraction (reactions (4k,l)) similar to the reaction of singlet methylene⁴³. Reactions (4q,r,s) represent production of CF_2 (which is important in the discussion below) and, finally, (4t) is the electronic quenching of O^* .

The estimated reaction rate⁸⁶ from equation 3 is $1.12 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ which is in adequate agreement with the experimental values listed in reference 86 ($0.95 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$).

The dynamics of this reaction has been studied by Lin⁶⁶ and by Addison *et al.*⁷⁰. Lin observed the HF laser emission that resulted when O₃ was flash photolysed in the presence of CHClF₂ and SF₆. Lin determined that the ratio of the populations in the $v'=2$ and $v'=1$ vibrational levels as a result of reaction was $N_2/N_1 \approx 0.8 \pm 0.02$. The total pressure used in that determination was 30 Torr with O₃:CHClF₂:SF₆ partial pressures in the ratios 1:1:20. As discussed in the previous two reactions, the ratio obtained by Lin could be affected by vibrational relaxation, particularly due to the partial pressure of CHClF₂ (a moderate relaxer of HF) as opposed to those of O₃ and SF₆ (both very poor at vibrationally relaxing HF). The presence of relaxation can be easily seen in Lin's results by the effect that the total pressure had on the laser intensity; as the total pressure increased, the laser intensity increased as well until it reached a peak at approximately 40 Torr and then rapidly decreased as the total pressure was further increased. The increase in laser intensity was due to the increased rotational relaxation of the HF as the amount of SF₆ was increased. The subsequent decrease in laser intensity was attributed to the enhanced vibrational relaxation due to the increased pressure of the halomethane. Vibrational relaxation must have also occurred at lower total pressures, although it was masked by the increase in intensity resulting from the rotational thermalization. Since the population ratios were obtained at a total pressure of 30 Torr while the HF laser intensity peaked at 40 Torr, it is expected that vibrational relaxation would have affected the distribution. As in the previous two reactions, Lin performed a mass spectroscopic analysis of the products. He states that products similar to those found in the previous reactions were found, although the results are not stated explicitly. Therefore it is expected that CO and CFCIO were found as products of this reactions.

In the investigation by Addison *et al.*⁷⁰, a number of halogenated methanes (of which only CHClF₂ is common with the reactants studied in this thesis) were individually

mixed with an excess of O_3 or N_2O and flash photolysed. The products CF_2 , ClO , and OH were monitored photographically by their absorption in the visible and near ultraviolet, and the amount of $O(^3P)$ produced was determined by its absorption at 130 nm. They determined that the yield of ClO was $55 \pm 10\%$, of CF_2 was $45 \pm 10\%$, of OH was 5%, of $O(^3P)$ was $28(+10-15)\%$ and of Cl -atoms was $\leq 10\%$. The sum of these products gives over 100% reaction and requires taking their lower limits to give a reasonable result of 98% yield, which leaves only 2% for the formation of HF . It is expected, therefore, that two (or more) of the products detected must be produced in the same one (or more) channel(s). Despite similar yields, ClO cannot be common with CF_2 since the formation of $ClO + CF_2 + H$ is endothermic by 176 kJ/mole. Addison *et al.* considered that CF_2 and $O(^3P)$ were produced in common (along with HCl) by reaction (4s) which is thermoneutral: using the enthalpies at 298.15 K and their uncertainties of reference 90, the heat of reaction for reaction (4s) is 17.47 ± 19.7 kJ/mole. Lin⁶⁶, however, found only HF emission and no evidence of HCl from this reaction. The substantially smaller Einstein A-factors for HCl (approximately 1/5 those for HF) could account for the absence of HCl laser emission in Lin's investigation: an HF/HCl ratio of 0.2 would make the two hydrogen halides equally detectable while a larger ratio favors detection of HF only. Using the lower values for the detected products found by Addison *et al.* and the assumption that CF_2 and HCl are produced together leaves a maximum of 15% of the reaction rate for HF production. This gives an upper limit to the HF/HCl ratio of 0.43 indicating that HCl could have been produced in conjunction with CF_2 (accounting for at least 35% of the reaction) but still be undetected by Lin.

The co-production of CF_2 , HCl , and $O(^3P)$ can explain the yields obtained by Addison *et al.* only if the lower limit for CF_2 and the upper limit for $O(^3P)$ production are used. In addition, the entire quenching channel (4t) would have to undergo subsequent

unimolecular decomposition into the desired products and would require the entire reaction exoergicity be resident in the molecular product (CHClF_2) for this to occur. This is not a feasible source of the CF_2 and suggests that there may be more than one channel contributing to the production of CF_2 . The only other energetically accessible channels leading to formation of CF_2 are (4q,r). Reaction (4r), thermoneutral within the errors of the enthalpies, can be achieved by two mechanisms; abstraction and insertion. Abstraction of OH, however, is typically a direct reaction and would impart insufficient energy into the polyatomic fragment, CF_2Cl , to induce its required decomposition into CF_2 and a Cl-atom. Insertion of the $\text{O}(^1\text{D})$ into the C-H bond can lead to channel (4r) in several ways. If the insertion and OH elimination is direct (short-lived) then it is not expected that sufficient energy will be contained in the CF_2Cl fragment to undergo the required unimolecular decomposition and channel (4j) will be the result rather than one of the channels producing CF_2 . A long-lived insertion intermediate, on the other hand, could be responsible for all three channels which produce CF_2 . Unimolecular decomposition of the excited alcohol into three fragments (reactions (4r,s)) is not expected to be very probable, but fragmentation into channel (4q) is and could serve as a precursor of the other two CF_2 producing channels: if the HOCl in reaction (4q) retains most of the reaction exoergicity, it can undergo subsequent unimolecular decomposition into channels (4r) and (4s).

From the above sources of CF_2 and the product yields of Addison *et al.*, it is expected that the majority of the detected CF_2 originated from reaction (4t) and that a small fraction of it was produced concurrently with (OH,Cl) or $(\text{HCl},\text{O}(^3\text{P}))$. This explanation is more satisfactory than that proposed by Addison *et al.* in that the quenching channel (4t) would no longer have to contribute its entire yield to co-production of CF_2 and the production of HCl could be sufficiently low to agree with the results of Lin⁶⁶ in which

only HF was observed. This explanation, however, requires that a substantial amount of the insertion into the C-H bond results in a long-lived intermediate that decays into channel (4q). This can be supported since the higher density of states in the triply halogenated methane would promote the dissipation of energy into the remainder of the intermediate and prolong its lifetime.

II.B.3.b Experimental Results: $O(^1D_g) + CHClF_2$

In this study, the O_3 and $CHClF_2$ had equal partial pressures of 5 mTorr each. The spectra observed from this reaction were taken with the earlier experimental arrangement. Five time delays were collected in all, at 50, 120, 200, 300, and 400 μs . The data collection for these time delays was not concurrent as in the previous two reactions and the spectra at the different time delays were not directly correlated. All measurements were, however, taken under similar experimental conditions of partial pressures and laser power which allows comparison of the results at different times. As a result, the spectra were analysed to give fractional populations rather than relative populations. Fractional populations are computed by rescaling the individual vibrational populations by their sum such that the sum of the resulting fractional populations is one for each time delay. Due to a laboratory mishap, none of the spectra can be reproduced, although a complete analysis was made and the results stated below.

HF emission was observed in the first measurement at 50 μs , corresponding to an average of 2.5 gas kinetic collisions of the HF with the ambient gas by the time of observation assuming that one collision was required for its production. The collision frequency for the experimental conditions was $6.9 \times 10^4 s^{-1}$. OH emission was not clearly observed at any time delay. Unanalyzable traces of OH were discernible, however, in the spectrum for the earliest time delay (which contained the largest number of coadded

interferograms). Neither HCl or CO were observed in any of the spectra, nor in the sum of all the spectra; in an attempt to find traces of HCl, all the spectra (for five different time delays) were added since the noise would increase by only the square root of the number of scans while any signal would increase linearly with the number of scans. In this way, it was expected that if the HCl signal were just under the detection limit for any one time delay, its signal (particularly in the low J states of $v' = 1$ which would be the largest in the sum) would reinforce and be detectable (although unanalyzable) thus giving an indication if HCl had been produced, even in very small quantities.

The fractional populations of the observed vibrational levels of the HF produced in this reaction are presented as a 3-dimensional plot in figure 44 and the values listed in table 8. The plot is similar to that previously described for the reaction with CH_3Cl , with the exception that the fractional population is plotted on the z-axis rather than the relative population.

The fractional populations of vibrational levels $v' = 1$ to 6 for the HF after 3.5 average gas kinetic collisions were 0.408, 0.218, 0.166, 0.103, 0.069, and 0.036. Each of the observed vibrational levels had a fully resolved rotational structure, with levels analyzable up to 25 for $v' = 1, 2$, and 3, to 19 for $v' = 4$ and 5, and 14 for $v' = 6$. For each of these vibrational levels, the rotational distributions were rather flat over their entire range with a distinct Boltzmann distribution already formed in the low J-levels of $v' = 1$ and a slight indication of one for $v' = 2$. The vibrational distribution is slightly more excited than expected if the HF were formed by a statistical decomposition, and has a slight inflection at $v' = 3$. Whether this inflection is physically significant or due to scatter of the points within the error of the experiment is unknown since the analysis program used for these results did not include error analysis. The distribution obtained

Figure 44: The time dependence of the fractional vibrational populations of the HF produced in the reaction $\text{O}^* + \text{CHClF}_2$. The time axis is given as $\langle Z_{gk} \rangle$, the number of gas kinetic collisions of the HF after the reaction was initiated. Each vibrational distribution is separately normalized to 1.0.

Table 8: Values of the fractional populations of each observed vibrational level of the HF from the reaction $O^* + CHClF_2$ for each time delay. The population for each vibrational level was obtained by summing the calculated populations of all the rotational levels with signal to noise greater than one belonging to that vibrational level. Error for these values were not calculated.

Delay	$\langle Z_{gk} \rangle$	$v' = 1$	2	3	4	5	6
1	3.5	0.4086	0.2177	0.1661	0.1027	0.0689	0.0350
2	8.3	0.3622	0.2908	0.2224	0.1057	0.0189	
3	13.9	0.4255	0.3267	0.2010	0.0467		
4	20.8	0.4709	0.3827	0.1464			
5	27.7	0.5166	0.3573	0.1261			

here did not agree well with that determined by Lin⁶⁶. Lin found the ratio between levels 1 and 2 to be $N_2/N_1 = 0.8$ while the same ratio from the present study was 0.53. This disagreement in the ratio was not considered to be serious, however, since Lin's result was obtained under experimental conditions for which relaxation would have affected the distribution as discussed previously for the CH_3Cl reaction.

The time evolution of the vibrational levels is given in figure 44 by the thick lines connecting the varying symbols for each v' -level and by their projection on the backplane. Again, it must be stressed that these are fractional populations and as such they represent the ratios between the populations of the levels rather than actual relative values. As a result, the slight drop in fractional population of level $v' = 1$ does not indicate a drop in the population of this level but rather that the ratio between its population and the sum of the populations in levels 2 to 4 had decreased at this time delay. This effect is consistent with normal vibrational relaxation where relaxation of the higher levels proceeds at a faster rate than that of the lower levels as is expected when the partial pressures of the reagents and their deactivation rates are considered.

Despite the lack of observable emission from HCl or OH , an estimation of the upper limit of their production was feasible. The total relative population of a vibrational level can be determined³⁰ in a diatomic from the population of any line, if a Boltzmann distribution is assumed, by the equation:

$$N_{v,J} = N_v (hcB/kT) (2J + 1) e^{-J(J+1)hcB/kT} \quad 7$$

where $N_{v,J}$ is the population of the J 'th level in vibrational level v , N_v is the population of the vibrational level v , h is Planck's constant, c is the speed of light, k is Boltzmann's constant, T is the temperature, and J is the rotational quantum number of the line

observed. From the actual analysis of the HF from this reaction, it was known that for the earliest time delay (3.5 gas kinetic collisions) high rotational excitation was observed and that only a small fraction of the population of each vibrational level had relaxed to a Boltzmann distribution, particularly for the higher vibrational levels. To test whether equation 7 could adequately determine the entire population of a vibrational level, it was used to calculate the fractional populations for all five time delays obtained for this reaction. The results are listed in table 9. The height of the P_3 line was measured and used to determine the population for each vibrational level. The P_3 line of HF was chosen since it would have originated from the rotational level with the greatest population in a Boltzmann distribution at 300 K. From the values listed in table 9, for the earlier time delays equation 7 slightly overestimates the populations in the lower vibrational levels and underestimates that of the higher ones. This trend was expected since rotational relaxation is faster for the lower levels and slower for the higher ones as evidenced by the appearance of a small Boltzmann distribution for the lower levels and none for the higher levels in the actual analysis for this time delay. For the last time delay (27.7 gas kinetic collisions) where all the observed population of each vibrational level had relaxed to a Boltzmann distribution, the fractional populations calculated from equation 7 and those from the actual analysis agreed within the expected errors of the two methods. From this comparison, it is expected that the use of equation 7 is suitable to estimate upper limits for the yield of HCl and OH by using the height of the noise in the spectrum at the appropriate wavenumber for the height of the HCl and OH lines. It must be noted that since all measurements are taken from a single spectrum for these calculations of relative branching ratios that the populations of different molecules are correlated. The greatest uncertainty in the estimations of the branching ratios lay in how many vibrational levels to consider for HCl and OH. The values chosen were five

Table 9: Comparison of the measured fractional populations and those calculated from equation 7 for the HF from the reaction $\text{O}^+ + \text{CHClF}_2$.

Time Delay	v' -level	Measured	Calculated
1	1	0.4086	0.525
	2	0.2177	0.266
	3	0.1661	0.107
	4	0.1027	0.046
	5	0.0689	0.031
	6	0.0361	0.025
2	1	0.3622	0.431
	2	0.2908	0.304
	3	0.2224	0.163
	4	0.1057	0.076
	5	0.0189	0.003
3	1	0.4255	0.473
	2	0.3267	0.326
	3	0.2010	0.162
	4	0.0467	0.039
4	1	0.4709	0.469
	2	0.3827	0.387
	3	0.1464	0.143
5	1	0.5166	0.509
	2	0.3573	0.390
	3	0.1261	0.101

vibrational levels for HCl (equal to the number observed in the reaction with CH₃Cl) and four for OH (again the number observed in the reaction with CH₃Cl). Since an *upper* limit for the branching ratios was sought, these values were chosen so that the populations of the HCl and OH would be over estimated but not drastically so. The branching ratios obtained from the calculations using equation 7 at 3.5 gas kinetic collisions were HF/HCl > 1.18 and HF/OH > 0.47. The values for the populations for all three molecules considered did not include that of $v' = 0$ since it is not observable in emission. The populations of HCl and OH were purposefully over estimated (by the inclusion of sufficient vibrational levels in the estimation) to ensure that these were valid *upper* limits.

II.C. Discussion: Experimental

II.C.1. General Discussion: Experimental

In the previous section, the HX vibrational distributions for all three reactions studied and the OH distributions for two of the reactions were presented. It must first be established that these distributions were indeed from the HX and OH produced from the primary reactions. In figure 45 the time evolution of the total observed populations of the HCl and OH detected in the reaction of O^* with CH_3Cl , and the HF and OH in the CH_3F reaction are plotted as a function of the number of gas kinetic collisions. The solid lines are a spline fit of the data for each product and the deviation of the lines from the points is indicative of the error in the points as previously discussed for figure 36. The values used for this figure are in tables 4, 5, 6, and 7 respectively. The total observed OH population from the reaction of O^* with CH_4 , the results of which has been reported in reference 76, is also plotted for comparison since these results were obtained using the same equipment. The time evolution is presented as a semi-log plot: an exponential decrease in the population will be reflected as a linear dependence with the slope proportional to the decay rate. From figure 45 it is apparent that there are two distinct patterns for the time evolution of the total populations. The time evolution of the HF in the CH_3F reaction decreases monotonically and shows a definite decrease over the time of observation. The total population of the OH observed in the CH_3F reaction decreased only slightly over the observation time of the experiment. All other total populations

Time Evolution of the Total Population

Figure 45: The time dependence of the total relative populations of the HF and OH produced in the reaction $O^* + CH_3F$, the HCl and OH in $O^* + CH_3Cl$, and OH in $O^* + CH_4$. The time axis is given as $\langle Z_{gk} \rangle$, the number of gas kinetic collisions of the product after the individual reactions were initiated.

presented in figure 45 displayed an increase and then decreased at a rate similar to that of the OH in the CH_3F reaction.

These differences in the total populations have several possible explanations. Since the total population of the HF in the CH_3F reaction displayed a distinctly different time evolution from the others in figure 45, any possible anomaly in its rate of decrease should be considered first. Only three loss mechanisms are available for the total population; vibrational relaxation into the non-emitting $v' = 0$ level, pumping of the reaction chamber and consumption in a secondary reaction. When the reactants and all the primary products listed in reactions (3a to k) are considered, there are no energetically accessible secondary reactions available to HF which discounts the third population loss mechanism. From calculations using the estimated HF vibrational relaxation rates specified in the previous sub-sections and the pumping rate (approximately $3 \times 10^3 \text{ s}^{-1}$), the continuous pumping of the reaction chamber is expected to be the major loss of population with a minor contribution from vibrational relaxation. Since the reported HF population was present from the first observation (2.6 gas kinetic collisions) and decreased at the expected rate, it is expected that it was produced entirely from the primary reactions (3a to e).

All other products for which correlated total populations could be calculated decreased at a substantially slower rate than that expected from the pumping speed. In particular, the total OH population from the reaction with CH_3F decreased at a noticeably slower rate than the total HF population from the same reaction. The vibrational relaxation of OH and HF by the gas mixture used in this investigation are expected to be of the same order of magnitude, therefore the pumping speed should be the major loss mechanism for the OH as well. There is no mechanism that can be envisaged that would preferentially

pump HF as opposed to OH. This leads to the conclusion that the measured OH population had an additional source during the experiment. There are two different sources which can contribute to the measured OH population. The first source is unobserved population in higher vibrational and rotational levels which relaxes into the levels used to calculate the total population. Reaction (3h) could populate up to $v' = 4$ and the total population was calculated using only levels $v' = 1$ to 3. If substantial population had been produced in $v' = 4$, it could account for the slow decrease in total population. This source of additional OH population is not considered to be sufficient for the observed slow rate of OH disappearance for two reasons. If sufficient population was produced in $v' = 4$ to provide the required additional total population, it would have been observable in the spectra despite the smaller Einstein A-factors for this level and would have been included in the calculated total population. Secondly, the rate of vibrational relaxation of OH is expected to increase with vibrational level, similar to the relaxation of HF and HCl, and could not have contributed to the observed levels over the entire time of the experiment (75 gas kinetic collisions for the last time delay) nor was there evidence in the time profile of the $v' = 3$ population (figure 42) of a substantial population in a higher level relaxing into it with a larger relaxation rate. Rotational relaxation is another possible source of 'hidden' population. If the population of a vibrational level is distributed amongst a large number of rotational levels, the intensity of each rovibrational line could be less than the noise in the spectrum and thus be unobservable. The OH detected in the CH_3F reaction was observable only after 19.7 gas kinetic collisions and only the low J-levels comprising a Boltzmann distribution were apparent. Assuming that the initial OH population was indeed distributed over a large number of levels, the appearance of the low-J Boltzmann distribution could have been due to the subsequent rotational relaxation of the initial distribution. It is difficult,

however, to expect rotational relaxation (which is typically at least gas kinetic or faster) to continue over the entire time of observation. Complete rotational relaxation had occurred by approximately 30 gas kinetic collisions for the HF and HCl detected from all the reactions studied and it is expected to be equally rapid for OH. In particular, the initial HF from this reaction had observable emission from rotational levels as high as $J = 26$ yet rotational relaxation was complete by the time delay corresponding to 31.6 gas kinetic collisions.

The second possible source of OH population over the time of the experiment is secondary reactions. Although a complete kinetic analysis of the possible reactions which can produce secondary OH was not made, there are several possible reactions readily found that can populate up to $v' = 2$ (*vide infra*).

The HF observed in the reaction with CH_3F is expected to be the result of the primary reaction. A similar expectation as to the source of the observed OH in this reaction can not be made if secondary reactions were responsible for the slower time evolution of its total population. The time evolution of the $v' = 3$ level does, however, display the proper time evolution and is expected to be due to the primary reaction. In addition, since all three observed vibrational levels remained undetectable until the fourth time delay (19.7 gas kinetic collisions) at which point only the rotationally relaxed Boltzmann distribution was apparent, it is expected that a substantial contribution to levels $v' = 1$ and 2 also came from the primary reaction (3h). Furthermore, the almost constant populations in levels $v' = 1$ and 2 indicates that the secondary reaction that produced OH populates only up to $v' = 2$.

A similar analysis of the HCl and OH detected in the reaction with CH_3Cl leads to similar conclusions. Again, the total populations of these two products decreased at a

slower rate than expected indicating that each had contributions from secondary reactions. The populations of each observed vibrational level of HCl from this reaction (figure 36) decreased more slowly than expected from the estimated relaxation rates and the pumping speed. This is particularly apparent when the time evolution of the HCl vibrational populations are compared with those of the HF from the reaction with CH_3F (figure 41). The pumping speed is the same in both experiments and the estimated vibrational relaxation rates for HCl are approximately five to ten times larger than those for the same levels of HF. Despite the expected faster vibrational relaxation of HCl, each HCl vibrational level decreased more slowly than the comparable level of HF. The limited data available from this experiment does not make it possible to unequivocally determine how many vibrational levels of HCl are populated by the secondary reaction. It is expected, however, that the initial HCl vibrational distribution at 2.7 gas kinetic collisions is produced entirely from the primary reactions (2 a to e). The only reagents present in sufficient concentrations to produce HCl prior to this measurement are O_3 , O^* , and $\text{O}_2(^1\Delta)$. O_3 can not be responsible for the secondary reaction since no dark reaction was observed as evidenced by the lack of detected signal in the zeroth time delay which was taken before the excimer laser fired. O^* is responsible for the primary reaction and the product concentrations from this reaction would be insufficient at 2.7 gas kinetic collisions to produce substantial amounts of HCl. The reaction of electronically excited oxygen, $\text{O}_2(^1\Delta)$, with CH_3Cl has not been investigated to date. Even though the production of HCl is energetically allowed for this reaction, it is not expected to be very fast and could not produce sufficient amounts of HCl to seriously affect the populations of the first time delay.

The OH population from the reaction of O^* with CH_3Cl has contributions from secondary reactions as well. Of the four vibrational levels observed, only $v' = 4$ displays

OF / DE

3

the time evolution expected for vibrational relaxation (figure 37). The other three observed vibrational levels, $v' = 1$ to 3, have time profiles incompatible with normal vibrational relaxation. The OH emission from this reaction was not detectable until the second time delay (8.6 gas kinetic collisions) and was comprised of the low-J Boltzmann distribution only. The $v' = 4$ level, which does not display a contribution from the secondary reaction, was not detected until the second time delay indicating that the initial OH population was rotationally excited and had to relax until sufficient population had accumulated in the lower rotational states for its emission to be detectable. Similar relaxation would have been required in levels $v' = 1$ to 3. The distinct increase in population for the third time delay, particularly in levels 2 and 3, is indicative of the increased importance of the secondary reaction by this time. As a result, the vibrational distribution at 8.6 gas kinetic collisions is expected to be principally due to the primary reaction (2h) with only a small contribution in levels $v' = 1$ to 3 from the secondary reactions.

The spectra from the reaction of O^* with $CHClF_2$ were not taken concurrently and the total populations from this experiment were not correlated. As a result, it can not be determined conclusively if secondary reactions affected the initial vibrational distribution calculated at 3.5 gas kinetic collisions. The time evolution of the fractional vibrational populations from this reaction (figure 44) when compared with that of the HF produced in the reaction with CH_3F (figure 41) appear very similar on the same time scale. Levels $v' = 1$ to 3 from the $CHClF_2$ reaction decrease more slowly than the comparable levels from the CH_3F reaction, although this could be due to differences in HF vibrational relaxation by $CHClF_2$ and CH_3F . Lacking incontrovertible evidence to the contrary, the initial distribution calculated at 3.5 gas kinetic collisions is expected to be entirely due to the primary reactions (4a to f).

The very similar late-time evolution of the total population for OH from CH_3F , HCl and OH from CH_3Cl , and OH from CH_4 is rather suspect. Without definite knowledge of the individual secondary reactions responsible for each of these products, this similarity can not be incontestably explained except as coincidence. A complete analysis of the possible secondary reactions has not been performed for any of the reactions. Secondary production of HCl in the reaction of O^* with CHCl_3 was reported by Aker *et al.*⁶⁹ and the suggested source was from the reaction of $\text{O}(^3\text{P})$ with one of the radicals produced in the primary reaction. If the secondary production in the reactions reported in this thesis involve $\text{O}(^3\text{P})$ and a radical from the primary reaction as well, they could all have similar, fast rates. A similarity in the secondary reaction rates for all of these products could possibly explain their similar time profiles.

II.C.2. Comparison to $O(^1D_g) + CHF_3$, $CHCl_3$ Results

The initial HX vibrational distributions obtained in this study are plotted in figure 46. In this figure, each distribution has been individually scaled so that the population in $v' = 1$ is equal to 1.0. Included in figure 46 are the initial vibrational distributions for the reactions $O^* + CHCl_3$, and CHF_3 , determined previously in this laboratory⁶⁹, at 14 and 5 gas kinetic collisions respectively. These five constitute the only measured vibrational distribution from the reaction of O^* with halogenated methanes in which the extent of vibrational relaxation can at least be estimated. From previous discussions, the HX distributions measured in this study are somewhat relaxed particularly in the higher vibrational levels and these represent lower limits to the initial distribution. A similar extent of relaxation should apply to the HF from CHF_3 . The HCl distribution from $CHCl_3$ was measured after considerably more collisions (14) than the others. This measurement, however, should not be seriously affected by relaxation for several reasons. First, the population is confined almost entirely to levels $v' = 1$ and 2 which, from estimated deactivation rates, relax much slower than the higher vibrational levels. In addition, $CHCl_3$ should have smaller deactivation rates than CH_3Cl due to the number of C-H bonds. From figure 36, levels $v' = 1$ and 2 of the HCl from reaction with CH_3Cl were only slightly affected by relaxation after 14 gas kinetic collisions, primarily due to relaxation into them from higher levels and minor contributions from secondary reactions. Relaxation of the HCl from $CHCl_3$ in these levels should be less indicating that the distribution measured by Aker *et al.* was not substantially relaxed.

The distribution in figure 46 show three distinctly different patterns. The HCl from $CHCl_3$ has very low vibrational excitation for the levels measured by Aker *et al.* When these results are combined with Lin's⁶⁵, the distribution in the first three vibrational

Figure 46: The initial relative vibrational populations of the HF and HCl produced in the reactions $\text{O}^* + \text{CH}_{4-m-n}\text{Cl}_m\text{F}_n$. The CHF_3 and CHCl_3 results are taken from reference 69. All populations are scaled to $v' = 1$ equal to 1.0. The lines connect the points corresponding to each reactant and do not represent a functional fit.

levels (scaled to $v' = 1$ equal to 1.0) is 2.0 : 1.0 : 0.2. Thus, for all vibrational levels populated by this reaction the distribution is monotonically decreasing with very little vibrational excitation. The other extreme in these distributions is the HF from reaction with CHF_3 . Again combining the distribution of Aker *et al.* with that of Burks and Lin⁶⁷, the relative populations of the first seven vibrational levels is 1.05 : 1.0 : 0.84 : 0.72 : 0.76 : 0.48 : 0.20. This distribution is substantially more excited than that of the HCl from CHCl_3 and is not monotonically decreasing: there is an inflection in the distribution at $v' = 4$. Aker *et al.* suggested that this inflection was due to two channels being operative for the production of HF: co-production of COF_2 in its ground (X^1A_1) state or in the first electronically excited (A^1A'') state which is stable. A similar inflection did not occur for the HCl produced in reaction with CHCl_3 since the excited (A^1A'') state of COCl_2 is strongly predissociative and formation of products on this upper COCl_2 surface would immediately revert to formation on the lower surface at an energy above any barrier to dissociation.

The third distribution pattern pertains to the HX formed by the three reactions presented in this thesis. Each of these have distributions that are more excited than that of the HCl from CHCl_3 yet less excited than that of the HF from CHF_3 . Although all three distributions appear quite similar for the levels determined in this study, when these results are combined with those of Lin⁶⁵ and Burks and Lin⁶⁷ for CH_3Cl and CH_3F respectively, differences in the vibrational excitation are apparent. These distributions for the first six vibrational levels are 1.64 : 1.0 : 0.84 : 0.50 : 0.26 : 0.12 for the HCl from CH_3Cl and 1.14 : 1.0 : 0.72 : 0.46 : 0.25 : 0.12 for the HF from CH_3F . These distributions are plotted in figures 38 and 43 respectively (with different scaling). Comparing these values, the HCl has less vibrational excitation than the HF. A similar comparison cannot be extended to the HF from CHClF_2 since a relative value for $v' = 0$

cannot be determined: Lin⁶⁶ did not measure the ratio between $v' = 0$ and 1, only between 1 and 2 in his study of this reaction. In figure 46, the distribution for the HF from CHClF_2 appears less excited than those of the HCl from CH_3Cl or the HF from CH_3F but this is not conclusive without a value for $v' = 0$. It would be consistent, however, for the vibrational excitation in the HX product to decrease as one progresses along the series $\text{CH}_3\text{F} - \text{CH}_3\text{Cl} - \text{CHClF}_2$ if the lifetime of the collisional complex increases with the density of states as found in the reactions of O^* with alkanes^{47,48,50}. A longer lifetime of the collision complex results in a greater percentage of the reaction exoergicity dissipating away from the reaction site and into the remainder of the collision complex thus reducing the available energy which can be channeled into vibration of the HX product. This explanation is not entirely satisfactory. The HF from reaction with CHF_3 is more vibrationally excited than the HF from CH_3F yet it should have a greater density of states in its collision complex and thus a longer lifetime.

The relatively greater vibrational excitation in the HF from CHF_3 could be due to co-production of $\text{COF}_2(\text{A}^1\text{A}'')$ in the electronically excited state. The geometry of the collision complex would favor production of the bent $\text{COF}_2(\text{A}^1\text{A}'')$ with a substantially shorter lifetime than for production of the linear $\text{COF}_2(\text{X}^1\text{A}_1)$ ground state which would require considerable adjustment of the angles in the collision complex or very high excitation of the bending mode. This can also explain the low vibrational excitation of the HCl from CHCl_3 since the $\text{COCl}_2(\text{A}^1\text{A}'')$ state is strongly predissociative. As a result, reaction into this channel would revert to reaction along the $\text{COCl}_2(\text{X}^1\text{A}_1)$ ground state potential while the HCl is still sufficiently close for interaction. This would delay formation of products until the exit channel for the ground state potential curves could be accessed. Aker *et al.* suggested that contribution of the electronically excited $\text{COF}_2(\text{A}^1\text{A}'')$ channel to reaction with CHF_3 was indicated by an inflection in the HF

vibrational distribution at $v' = 4$, the maximum level energetically allowed for this channel. Slight inflections in the initial HX vibrational distributions also occur for reaction with CH_3Cl (figure 38), CH_3F (figure 43), and CHClF_2 (figure 46) at $v' = 2, 1$, and 3 respectively. These inflections are much less pronounced than the one in the HF distribution⁶⁹ from CHF_3 and could be merely variations within the errors of the individual distributions. They are, however, consistent with the expected energetics of the excited carbonyl in each of these reactions. Discussion of the excited state channel in these reactions is complicated by the nature of the excited carbonyls formed. They are neither strongly predissociative as in the case of $\text{COCl}_2(\text{A}^1\text{A}'')$ nor stable as in the case of $\text{COF}_2(\text{A}^1\text{A}'')$ but lie somewhere between these extremes. The excited carbonyl produced during HX formation in reaction with both CH_3Cl and CH_3F is $\text{CH}_2\text{O}(\text{A}^1\text{A}'')$. This electronic state of formaldehyde³¹ is weakly predissociative above 28736 cm^{-1} and its absorption bands become diffuse around 275 nm. Taking the onset of diffuseness to indicate the energy below which $\text{CH}_2\text{O}(\text{A}^1\text{A}'')$ is semi-stable, then reaction into the excited carbonyl channel is energetically capable of producing $\text{HCl } v' = 2$ (but not quite 3) from CH_3Cl and $\text{HF } v' = 2$ from CH_3F . These maximum allowed vibrational levels for reaction producing the electronically excited carbonyls correspond quite well with the level at which the slight inflection occurred in the HX vibrational distributions for these two reactions. For the CHClF_2 reaction, the excited state carbonyl, $\text{FCICO}(\text{A}^1\text{A}'')$, predissociation starts¹⁰⁰ at 235 nm, although it was not stated whether this was weak or strong predissociation. The enthalpy of this level is not known and was estimated to determine the exothermicity of this reaction channel. Using the estimated enthalpy of this state and the energy at which predissociation begins, the HF produced in this excited carbonyl reaction channel could populate up to $v' = 1$. Uncertainties in the enthalpy and the wavelength at which strong predissociation begins could easily extend the maximum

HF vibrational level which can be populated by this channel to $v' = 2$, which would coincide with the level at which the inflection occurred in the HF vibrational distribution. The contribution of the excited state channels in these reactions cannot be quantitatively determined, although their influence on the initial vibrational distributions is suggested.

That these reactions have a contribution from a semi-stable excited state carbonyl similar to COF_2 below a certain energy and a strongly predissociative excited state carbonyl similar to COCl_2 above it, indicates that their vibrational distributions would have characteristics of the high excitation found in the HF from CHF_3 as well as the low excitation found in HCl from CHCl_3 . This would produce HX from these reactions with vibrational excitation lying between the two extremes, as was observed. The three reactions presented in this thesis have varying degrees of excitation. Whether this is due to differences in the dynamics of producing the excited carbonyl or the density of states in the ground and excited state collision complex cannot be ascertained due to the complexity of the carbonyl predissociations.

The dynamics of these reactions must also account for the observed OH/HX branching ratios. These are 105, 46, and <2 (HF) for reaction with CH_3Cl , CH_3F , and CHClF_2 respectively and ~ 0.2 and <0.8 for CHCl_3 and CHF_3 as estimated by Aker *et al.*⁶⁹. The first two are consistent with the ratios expected from bond additivity⁷⁰ as expressed in equation 3. From the arguments presented in the overview for these two reactions (sections II.B.2.a and II.B.3.a), if bond additivity is valid then the large OH/HCl ratio in reaction with CH_3Cl supports the premise that ClO is a major channel and the OH/HF ratio from CH_3F indicates that the contribution to reaction by C-F bonds (given as $0.03 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ by Addison *et al.*⁷⁰) is too large and should be closer to $0.014 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. It must be stressed that the branching ratios for these

reactions have large errors due to the low intensities of the OH emission lines. In addition, a large number of assumptions were made in the overviews of these reactions to allow estimates of the branching ratios from equation 3. The measured ratios do, however, support the validity of bond additivity in these two reactions and the expectation that reaction at the C-Cl bond to form ClO is the dominate channel for CH_3Cl .

The very small OH/HX branching ratios in the triply substituted methanes are difficult to reconcile with the expected mechanisms for OH and HX production. Of the mechanisms that can produce OH, the two most important ones are expected to be abstraction and insertion-elimination. Insertion is expected to be the first step in HX elimination as well, followed by release of the H-atom which subsequently interacts with one of the halogen atoms and finally the HX is eliminated. In CH_4 , production of OH is approximately 80% of the reactivity⁵⁶ while H-atom substitution and H_2 elimination account for about 13% together. From the branching ratios for CH_3Cl and CH_3F above, it is also seen that OH formation greatly exceeds that of HX. The small branching ratios for the triply halogenated methanes indicate that OH production is a much less important channel in these reactions. The relatively large size of the halogen atoms could act as a steric hindrance to insertion into the C-H bond and would decrease the amount of OH produced by this mechanism. This would, however, have two other consequences. Those collisions that would have inserted into the C-H bond will now either interact with the closest halogen and form a halogen oxide or react with the C-H bond by abstraction. The latter occurrence would increase the amount of OH production and partially counter the initial reduction of OH elimination by insertion. In addition, if insertion into the C-H bond is hindered, H-atom substitution (the precursor of HX production) will decrease. The overall effect of such a steric hindrance would be an increase in OH production over

that of HX rather than the desired effect. On the other hand, if insertion into the C-H bond is not hindered, there is no apparent reason why substitution of the H-atom should be favored over OH elimination opposite to what is observed in CH₄, CH₃Cl, and CH₃F.

There is one mechanism that can be envisioned which could serve to enhance HX production. This mechanism has not previously been suggested for this class of reaction and is therefore highly speculative. The impetus behind this mechanism is that in a triply substituted methane, any collision with the correct angle of approach to insert into the C-H bond must also be in the vicinity of a halogen atom. Halogen atoms have much larger radii than a hydrogen atom and have greater bond lengths in these methanes (approximately 0.175 and 0.133 nm for C-Cl and C-F respectively as opposed to 0.11 nm for C-H in these triply substituted methanes⁹⁰). As a result, interaction with the C-X bond may occur before the O^{*} atom is sufficiently close to the C-H bond for the preferred, more energetic interaction can be established. This could lead to *insertion into the C-X bond*, a mechanism that has been considered not to occur in previous studies of O^{*} reactions with halomethanes or singlet methylene reactions with singly chlorinated alkanes. The impulse given to the halogen atom as the C-X bond stretches to accommodate the O^{*}-atom may be sufficient to expel it from the collision complex and 'pick-up' the highly mobile H-atom as it leaves. In this way, the OH abstraction component remains the same as in other methanes while the collisions that usually proceeded by insertion into the C-H bond are now C-X insertions leading to HX elimination. Since C-H insertions are considered to comprise a large fraction of the OH yield, this would greatly decrease the amount of OH produced while greatly increasing the amount of HX. This mechanism is neither substantiated nor refuted by any of the results given previously. The energetics and final products are not altered by this proposed mechanism and all arguments about the initial vibrational excitation hold

equally well here as when insertion into the C-H bond was assumed to be the responsible mechanism.

II.C.3. Comparison to $O(^1D_g) + CH_4$ Results

The 'initial' vibrational distributions of the OH produced in reaction with CH_3Cl and CH_3F are plotted in figure 47. The initial distribution⁷⁶ from reaction with CH_4 is presented as well. Internal state distributions have not previously been measured for the OH produced in the reaction of O^* with halogenated methanes and comparison is restricted to these three molecules. Luntz determined that for vibrational levels 1 and 2, 95% of the OH was produced by insertion and 5% by abstraction. The ratio of the populations in these two levels was 1.0 from each of these mechanisms indicating that the populations in the first two levels were equal. The initial relative populations in levels $v' = 1, 2, 3$, and 4 have been determined in this lab and reported in reference 57. These results have been reproduced as a three dimensional plot in figure 48 following the same conventions as described for figure 36.

As indicated earlier in the discussion, the total population did not decrease at the expected rate and indicated the presence of secondary reactions. From the time profiles of the individual vibrational levels (figure 48), the influence of secondary reactions is quite apparent. None of the levels relax vibrationally at the expected rates for OH under the experimental conditions, indicating that the secondary reactions can populate at least up to $v' = 4$. The distinct increase in populations from the first (3.4 gas kinetic collisions)

Figure 47: The initial fractional vibrational populations of the OH produced in the reactions $\text{O}^* + \text{CH}_{4-m-n}\text{Cl}_m\text{F}_n$. The CH₄ population is taken from reference 76. The lines connect the points corresponding to each reactant and do not represent a functional fit.

Figure 48: The time dependence of the relative vibrational populations of the OH produced in the reaction $\text{O}^* + \text{CH}_4$. The values for this figure were taken from reference 76. The time axis is given as $\langle Z_{\text{gk}} \rangle$, the number of gas kinetic collisions of the OH after the reaction was initiated.

to the second time delays indicates the onset of the secondary reactions, therefore, the distribution at the earliest time delay should represent the OH produced from CH₄.

Each of the vibrational levels represented in figure 48 had fully resolved rotational lines with observable emission at the first time delay from levels almost up to the maximum energetically allowed with a slight indication of a low-J peak for each vibrational level. Luntz attributed the low-J peak in his measurements to the abstraction component and the broad high-J rotational distribution to insertion. A similar assignment to the results obtained in this lab is difficult since the degree of rotational relaxation is unknown. Rotational relaxation in the HX observed from the reactions reported in this thesis was minor before the first time delay and apparent in $v' = 1$ and 2 only. If OH has a similar rotational relaxation in these experiments then the occurrence of a low-J peak for all vibrational levels at the earliest observation time as well as a broad high-J distribution indicates that abstraction and insertion both contribute to each observed vibrational level.

The initial OH distribution from reaction with CH₃Cl appears to be bimodal, although, within the error of the individual levels, it may simply be inverted. This distribution is for 8.5 gas kinetic collisions and consisted only of a low-J peak. There are two interpretations possible; abstraction was the only mechanism operative in the OH production and the high-J population from insertion was never there *or* the high-J rotational population had completely relaxed to a Boltzmann distribution and made an undetermined contribution to the low-J peak. The OH was not observed until the second time delay, therefore it is expected that the latter explanation pertains. It cannot be determined whether all of the low-J peak was due to relaxation of the insertion component or if it was also, in part, due to abstraction.

The initial OH distribution from reaction with CH_3F appeared to be inverted although the error in each level was very large. This distribution was obtained after 19.5 gas kinetic collisions and rotational relaxation would have been substantial. Only a low-J peak was observed and it was attributed to a Boltzmann distribution resulting from relaxation. As discussed previously, there are indications that secondary reactions contribute to the OH observed in this reaction. The large number of collisions prior to measurement of this distribution makes the extent of secondary reactions contributing to it quite uncertain. It is, however, expected that the major contribution to this distribution is from the primary reaction. Due to secondary reaction, this distribution will not be discussed further, particularly since some of the candidate secondary reactions are expected to proceed by abstraction reactions and would preferentially populate the low-J levels that are observed.

The OH from all three reactions, CH_3Cl , CH_3F and CH_4 , have inverted distributions. This indicates very high vibrational excitation and that the OH observed from these reactions was primarily produced by a direct mechanism with a short-lived intermediate. OH abstraction from methanes by O^* is expected to be direct since the collision complex thus formed is not a stable molecule. The insertion mechanism is also expected to be direct due to the short lifetime⁵⁶ of the methanol intermediate. The separate contributions from insertion and abstraction cannot be determined for any of these reactions due to rotational relaxation. Despite the apparent differences in these three distributions, within the errors of the individual distributions, they are the same. Within the error limits of these results, halogen substitution in methane has no effect on the initial OH vibrational distribution.

II.C.4. Comparison to $O(^1D_g) + HD$ Trajectory Calculations

In the first section of this thesis, the results of trajectory calculations for the reactions $O^* + H_2$, HD, and D_2 were presented. These trajectory calculations, particularly those for HD, were performed, in part, to provide some insight into the dynamics governing OH production in halogenated methanes. The monotonically decreasing vibrational distributions for the OH product from reaction with HD starting with eigenvalue 1, figure 19, do not resemble the inverted distributions determined for the halogenated methanes, figure 47. This lack of correspondence probably results from the D-atom being insufficiently heavy to emulate the massive halogenated alkyl. It was shown that insertion into H_2 is facilitated by the capability of the light H_2 molecule to reorient itself to an insertion geometry even when the initial approach is nearly 'end-on' (figure 7). The relatively light HD molecule is still sufficiently mobile to be rapidly reoriented during the collision and insertion remains the dominate reaction mechanism. The heavy halogenated methanes cannot reorient rapidly and abstraction is a competitive mechanism.

There is a similarity, however, between the OH distributions from the halogenated methane reactions and the eigenvalue 2 trajectory results. The potential surfaces for these two sets of reactions are very similar. In each, it is the $^1\Pi$ surface in the collinear abstraction configuration that correlates with the ground state products. If OHR has a similar ordering of states in the entrance channel as has OHH then a similar curve crossing would also occur and there should be a barrier on the $^1\Pi$ surface. The height of this barrier is not known. If it is sufficiently small, then reaction on the $^1\Pi$ eigenvalue 2 surface of OHR could be a major reaction channel with its attendant inverted vibrational distribution. It may be *this* reaction channel to which the halogenated methane OH

vibrational distributions should be compared. Based on this supposition, the agreement between the trajectory calculations and the experimental OH distributions is quite good.

II.D. Conclusions: Experimental

The initial vibrational distributions of the HX and OH from the reactions of $O(^1D_g)$ with CH_3Cl , CH_3F , and $CHClF_2$ have been measured (in the reaction with $CHClF_2$, only HF emission was observed). The HX distributions were all monotonically decreasing and more excited than expected if they were produced by a statistically governed decomposition of a long-lived collision complex. The high rotational excitation apparent in the spectra obtained at the earliest observation times indicated that the H-atom left the collision complex first and subsequently interacted with a halogen to form HX. The vibrational and rotational distributions were consistent with HX production being the result of O^* insertion into a C-H bond.

The HF from reaction with CH_3F had the greatest vibrational excitation and the HF from $CHClF_2$ had the least with the HCl from CH_3Cl in between. The amount of vibrational excitation in the HX from the individual reactions had two contributing factors. Firstly, the density of states in the collision complex increased the lifetime of the collision complex and reduced the vibrational excitation. Secondly, HX could be formed by two separate channels; one co-producing the ground electronic state of the carbonyl and the other the first excited state. Each of the excited state carbonyls produced in these reactions was predissociative and the energetics of their predissociation would affect the vibrational distributions. The involvement of the excited state was indicated by a slight

inflection in the vibrational distributions, as previously suggested by Aker *et al.*⁶⁹ in the reaction with CHF_3 . The extent that each of these contributed to the vibrational excitation could not be determined.

The initial vibrational distributions of the OH produced in reaction with CH_3Cl and CH_3F were inverted. Each distribution was comprised of an abstraction and an insertion component, although the separate contributions from these two mechanisms could not be determined.

The OH/HX branching ratios in the reactions with CH_3Cl and CH_3F agreed with their expected values as determined by the expression for bond additivity given by Addison *et al.*⁷⁰. This did not constitute proof of the validity of bond additivity but did demonstrate its usefulness. The OH/HF branching ratio in the reaction with CHClF_2 was substantially lower than expected. The reason for this is not understood.

The HX and OH from each of these reactions (except HF from CHClF_2) showed contributions from secondary reaction at later times. No attempt was made to identify these secondary reaction, although several candidates can readily be found in each case.

The OH vibrational distributions from the halogenated methane reactions and the *eigenvalue 2* trajectory results were in good agreement. This adds impetus to the need for improved multi-surface trajectory calculations and an understanding of the dynamics of *eigenvalue 2* reactions. It also accentuates the need for good multi-surface *ab initio* calculations for these reactions.

Appendix A.1.

Throughout this thesis, product state distributions are compared to a statistical distribution, that is, the distribution expected from phase space considerations alone with no dynamical effects included. This distribution is termed the 'prior' distribution and is defined as¹⁹:

$$P^o(v',J') = (2J' + 1) \rho_T(E - E_i') / \sum ((2J' + 1) \rho_T(E - E_i')) \quad A1$$

where $P^o(v',J')$ is the probability of populating state (v',J') , $\rho_T(E - E_i')$ is the density per unit interval of translational states at an energy of $(E - E_i')$ where E is the total energy available to the products and E_i' is the energy partitioned to the internal quantum states of the products, and the summation is over all available (v',J') states. The vibrational prior distribution, $P^o(v')$ is obtained by summing over all available J' states. Assuming that the diatomic product can be approximated as a vibrating rotor, then $P^o(v')$ can be approximated as:

$$P^o(f_v) = B_v^{-1} (1 - f_v)^{3/2} / \sum B_v^{-1} (1 - f_v)^{3/2} \quad A2$$

where f_v is the reduced energy variable (E^v/E) and the summation is over all accessible vibrational states.

For the reaction $O^* + H_2$ at an initial translational energy of 0.084 eV, and initial internal quantum states $v = 0$ and $J = 0$, the OH vibrational distribution obtained from the trajectory calculations and from equation A2 (the prior distribution) are:

v' level	Prior	Traj. Calc'n.
0	1.000	1.000
1	0.704	0.897
2	0.431	0.557
3	0.195	0.321
4	0.027	0.125.

Appendix A.2

Listing of the OH population analysis program. The external subroutine SPOFS was obtained from the SLATEC library⁷⁸.

```

PROGRAM POPDM
CHARACTER*1 ANS,IR,JRV,JRA,PRTY,PRTYX,SLBL,C3,C2,IX
CHARACTER*3 MLCUL,MDV,LBL,MDV4
CHARACTER*4 LPLBL
CHARACTER*4 PM,PGSTY
CHARACTER*12 DATE
INTEGER*2 I2(250),I2ADV(2,5)
INTEGER*4 VLU,FLAG,SCNS,SCRT,ASSGN,VMIN,VMAX,VLBL,VUP,VUPX,OVL
INTEGER*4 PFLAG,PFLAG,PFLAG,OVFLAG,VX,MDVAL
REAL MDPTS,JLST,MAXI,MINI,MAXL
DIMENSION VLU(50),SRV(50),JLNN(50),JLNN(50)
DIMENSION PTS(15+00),MDV(15+00)
DIMENSION PREQ(1,50),SORT(0:50,10,3,4)
DIMENSION JR(1+50),VUP(1+50),JLON(1+50),JST(1+50),PRTY(1+50)
DIMENSION APAC(1+50),JLST(15+00),PCI(1+50),VLSGN(1+50)
DIMENSION ASSGN(2,10,3),OVL(6,1+50)
DIMENSION VMIN(3),VMAX(3),JMIN(3),JMAX(3),JL(10)
DIMENSION JLBL(0:50),VLBL(10),LJBL(4),PPLJL(4),JLBL(3)
DIMENSION POPB(3,4),POPE(3,4)
DIMENSION POPV(10,3,4),POPE(10,3,4),PVAX(10,3,4)
DIMENSION POPL(0:50,10,3,4),POPL2(0:50,10,3,4)
COMMON/AT50/ JLST,VUP,JLON,JST
COMMON/CHARS/ IR,PRTY
COMMON/OSXV/ PSCL,PRQ,SORT
COMMON/OVLP/ VMIN,VMAX,ASSGN,OVL
COMMON/AT5K/ AVRG,YRMDV,PES,MDV
DATA SLBL/'P','Q','R',/LJBL/'3/2','3/2','1/2','1/2',/MDV/'MDV'/
DATA VLBL/1,2,3,4,5,6,7,8,9,10,/PPLJL/'3/2+','3/2-','1/2+','1/2-'/
DATA JLBL/0,1,2,3,4,5,6,7,8,9,10,11,12,13,14,15,16,17,18,19,20,21,
122,23,24,25,26,27,28,29,30,31,32,33,34,35,36,37,38,39,40,41,42,43,
244,45,46,47,48,49,50/
1000 FORMAT(A1)
1005 FORMAT(1A,A1)
1010 FORMAT(A12)
1015 FORMAT(1X,'DATE',5X,A12)
1020 FORMAT(A5)
1030 FORMAT(1X,'PROCESSING FILE ',A3)
1040 FORMAT(A3)
1045 FORMAT(1X,'MOLECULE ',A3/1X,'FILE',3X,A6/1X,'LIBRARY',A3)
1050 FORMAT(1X,'SPECIAL REGION TO BE SEARCHED IN CH-17 (76.1,1X,73.1)'
1)
1060 FORMAT(76.1,1X,73.1)
1065 FORMAT(1X,'REGION ',76.1,' - ',73.1,' CH-1')

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1070 FORMAT(1X,'WHAT LINES ARE TO BE ASSIGNED?'/1X,
1' INPUT V(UPPER)-BRANCH, AND RANGE OF J(LOWER) VALUES FOR EACH'/1X,
2' LEVEL AND BRANCH TO BE USED IN "ASSIGNING" LINES.'/1X,
3' I.E. 01P 01,10 (I2,A1,2(1X,I2)) TO END INPUT,TYPE " D"<CR>')
1075 FORMAT(///1X,'ASSIGNED TRANSITIONS'/)
1080 FORMAT(I2,A1,2(1X,I2))
1090 FORMAT(4X,I2,A1,I2,' TO ',I2)
1100 FORMAT(/1X,'IF THIS IS NOT CORRECT THE ENTIRE LIST MUST BE',1X,
1' RE-ENTERED.'/1X,'ARE THESE THE TRANSITIONS YOU WANT ASSIGNED?',
2' (Y/N)')
2005 FORMAT(I3)
2010 FORMAT(I4,2X,A3,F10.4)
2020 FORMAT(10F7.4)
2030 FORMAT(1X,'THIS SPECTRUM IS BEING PROCESSED FOR THE FIRST TIME'/
11X,'ARE THERE ANY LASER SPIKES TO BE REMOVED? (Y/N)')
2040 FORMAT(1X,'INPUT THE NUMBER OF SPIKES TO BE REMOVED (MAXIMUM OF',
1' 5) AND THE'/1X,'START AND END POINTS (IN CM-1) FOR EACH ONE.',
2' I1,N(1X,F6.1))')
2050 FORMAT(I1,10(1X,F6.1))
2055 FORMAT(///1X,'THIS SPECTRUM WAS A RAW SPECTRUM. THE FOLLOWING',I2,
1' REGION(S) WERE SLG'D:',5(1X,F3.1,' TO ',F3.1))
2060 FORMAT(1X,I1,' LASER SPIKES HAVE BEEN REMOVED, ANY MORE? (Y/N)')
2070 FORMAT(/1X,'THIS SPECTRUM IS THE RESULT OF',I4,' CO-ADDED SPECTRA,
1'REPRESENTING',I5,' COMPLETE SCANS.'/1X,'THE AVERAGE VALUE BETWEEN
2200. AND 3950. CM-1 (BEFORE RDV) IS',F11.4)
2071 FORMAT(/1X,'THE AVERAGE VALUE BETWEEN 2200. AND 3950. CM-1 (BEFORE
1 RDV) IS',F11.3)
3000 FORMAT(I1)
3010 FORMAT(///1X,'MINIMUM INTENSITY IS',F3.4,' AT',F3.1,' CM-1'/1X,
1' AND MAXIMUM INTENSITY ABOVE THIS IS',F3.4,
2' (IN PROGRAM UNITS), AT',F3.1,' CM-1.')
4010 FORMAT(F11.4,2X,A1,F3.3,I3,2F5.1,A1)
4020 FORMAT(//1X,'***** WARNING ***** LINE',I3,A1,I2,F4.1,A1,' AT',
1F7.1,' IS NOT IN THE SPECIFIED SPECTRAL WINDOW. IT WILL NOT BE',
11X,'ASSIGNED'/)
4025 FORMAT(/1X,'BRANCH',I3,A1,' IS TOTALLY OUTSIDE THE SPECIFIED '/1X,
1' SPECTRAL WINDOW. RE-ENTER THE ENTIRE LIST OF TRANSITIONS TO BE',
21X,'ASSIGNED'/)
4030 FORMAT(/1X,I3,' LINES SATISFY ALL SPECIFICATIONS')
4040 FORMAT(//1X,'THE LIBRARY HAS BEEN SORTED AND THE TRANSITIONS ',
1' THAT ARE INCLUDED'/1X,'IN THE CATALOGUE (LIE WITHIN THE SPECTRAL'
2,1X,'WINDOW) ARE:')
4050 FORMAT(4X,I2,A1,I2,' TO ',I2)
5010 FORMAT(/1X,'MAXIMUM LINE COULD NOT BE IDENTIFIED.'/1X,
1' NO TRANSITION LIES WITHIN ',F4.2,' CM-1'/1X,'OF THE LINE WITH',
21X,'MAXIMUM INTENSITY AT ',F6.1,' CM-1.')
5020 FORMAT(/1X,'MAXIMUM LINE IDENTIFIED AS ',I2,A1,I2,1X,F3.1,A1/1X,
1' IS THIS CORRECT? (Y/N)')
5030 FORMAT(/1X,'INPUT MAXIMUM LINE: V(UPPER)-BRANCH-J(LOWER) E(STATE)'
1,'-PARITY'/1X,'EXAMPLE 02P05 1.5+ (I2,A1,I2,1X,F3.1,A1)')
5040 FORMAT(I2,A1,I2,1X,F3.1,A1)
5050 FORMAT(1X,I2,A1,I2,1X,F3.1,A1)

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6010 FORMAT(1X,'THE FOLLOWING LINES ARE OVERLAPPED:')
6020 FORMAT(1X,'LINE TRANSITION      OVERLAP VECTOR')
6030 FORMAT(1X,I3,2X,I2,A1,I2,F4.1,A1,2X,6I4)
6040 FORMAT(1X,'THERE ARE NO OVERLAPS.')
6050 FORMAT(//1X,'SORT ARRAY')
6060 FORMAT(1X,A4,2X,A1,I3,10I6,4(//1X,10I6))
7010 FORMAT(//1X,'THE MAXIMUM LINE ',I2,A1,I2,1X,F3.1,A1,1X,
1'IS OVERLAPPED WITH THE FOLLOWING ',I3,' LINE(S):')
7020 FORMAT(I2,A1,I2,1X,F3.1,A1)
7025 FORMAT(1X,I2,A1,I2,1X,F3.1,A1)
7030 FORMAT(1X,'IS THIS ACCEPTABLE? (Y/N)')
7040 FORMAT(1X,'INPUT MAXIMUM LINE: V(UPPER)-BRANCH-J(LOWER) E(STATE)
1,'-PARITY'/1X,'EXAMPLE 02P05 1.5+ (I2,A1,I2,1X,F3.1,A1)')
7050 FORMAT(1X,'THE MAXIMUM LINE BEING CONSIDERED HAS BEEN AVERAGED IN
1TO THE LINE'/1X,'THAT IS THE SAME STATE BUT DIFFERENT PARITY. WILL
2 ATTEMPT'/1X,'TO LOCATE IN THE CATALOGUE THE LINE THAT IT HAS BEEN
3 AVERAGED INTO')
7060 FORMAT(1X,'THE LINE THAT WILL BE USED AS THE MAXIMUM IS ',I2,A1,
1I2,1X,F3.1,A1)
8010 FORMAT(///1X,'SHOULD ANY LINES BE ADJUSTED FOR ABSORPTION? (Y/N)')
8020 FORMAT(1X,'FOR EACH LINE INPUT: V(UPPER)-BRANCH-J(LOWER) E(STATE)
1,'-PARITY'/1X,'AND THE FACTOR BY WHICH THE PRESENT INTENSITY (RDV
2'D AND MEASURED FROM THE LOCAL BASELINE)'/1X,'SHOULD BE',1X,
3'MULTIPLIED BY. (I2,A1,I2,1X,F3.1,A1,1X,F4.2) IE 01P02 1.5+ 1.21',
4'/1X,'TO TERMINATE, INPUT " D"<CR>')
8025 FORMAT(///1X,'THE FOLLOWING LINES HAVE BEEN ADJUSTED FOR ABSORPTIO
1N: '//1X,'TRANSITION FACTOR')
8030 FORMAT(I2,A1,I2,1X,F3.1,A1,1X,F4.2)
8040 FORMAT(1X,I2,A1,I2,F4.1,A1,F7.2)
9001 FORMAT(//1X,'** POPON ** LINE',I4,' (TRANSITION',I3,A1,I2,F4.1,A1,
1' A',F5.2,') PASSED TO OVRLP '//1X,'** OVRLP **')
9003 FORMAT(///1X,'ANALYSIS: '//1X,'LINE TRANSITION FREQ POINT',2X,
1'Y-VALUE LCL MIN ABSN INTNSTY A-FACT POP*N ERROR')
9007 FORMAT(1X,I3,I3,A1,I2,2X,F3.1,A1,F7.1,I6,2F9.4,F5.2,F9.4,3F8.3)
9009 FORMAT(1//1X,'NORMALISED RESULTS: '//)
9010 FORMAT(14X,'E-STATE=',A3//)
9020 FORMAT(' ',A1,' BRANCH',/)
9030 FORMAT(2X,'J LOW',2X,10(I2,10X),4(//7X,10(I2,10X)))
9047 FORMAT(' V=',I2,10(F6.3,':',F5.3),4(//3X,10(F6.3,':',F5.3)))
9048 FORMAT('/' All values scaled by ',F3.2,' ie POPN=',F3.2,
1'REAL POPN')
9050 FORMAT(//7X,'LEVEL POPULATION FRACTION OF BRANCH POPULATION')
9060 FORMAT(' ',V=',I2,F5.4,' +- ',F8.4,5X,F7.3,' +- ',F7.3)
9070 FORMAT(//5X,F5.4,' +- ',F8.4,' = SUM FOR BRANCH')
9080 FORMAT(' ',3X,'V=',5(4X,I2,4X),(//8X,5(4X,I2,4X)))
9090 FORMAT(' ',J=',I2,1X,5(2X,F6.5),(//3X,5(2X,F6.5)))
9100 FORMAT(// ' POPN ',5(2X,F5.5),(//5X,5(2X,F5.5)))
9105 FORMAT(2X,'+- ',5(2X,F5.5),(//4X,'+- ',5(2X,F5.5)))
9110 FORMAT(1X,'ALTER ANY LEVELS? (Y/N)')
9120 FORMAT(1X,'FOR EACH LEVEL TO BE CHANGED, INPUT V(UPPER)-BRANCH-J(L
10W24) AND THE'/1X,'NEW VALUE TO BE USED AS THE POPULATION. I2,A1,I
22,F7.3) IE 01P03 56.900'/1X,'TYPE " D"<CR> TO TERMINATE INPUT')

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9125 FORMAT(///1X,'THE FOLLOWING LINES HAVE BEEN MANUALLY ALTERED: '/')
9130 FORMAT(I2,A1,I2,F7.3)
9135 FORMAT(//1X,'NOT A LINE IN THE ABOVE CALCULATION. TRY AGAIN')
9140 FORMAT(1X,I2,A1,I2,F7.3)
9500 FORMAT(1X,'DATE ',A12,' FILE ',A5,' MOLCL ',A3)
9501 FORMAT(I4,' SMOOTHING PARAMETER: 0=NO,1=5 PT,2=9 PT,3=17PT')
9502 FORMAT(1X,3(2X,I3),5X,'BRANCH ANALYSIS: START, FINISH AND STEP')
9503 FORMAT(1X,3(2X,I3),5X,'VMIN FOR BRANCHES P, Q, AND R')
9504 FORMAT(1X,3(2X,I3),5X,'VMAX FOR BRANCHES P, Q, AND R')
9505 FORMAT(1X,3(2X,I3),5X,'JMIN FOR BRANCHES P, Q, AND R')
9506 FORMAT(1X,3(2X,I3),5X,'JMAX FOR BRANCHES P, Q, AND R')
9507 FORMAT(5X,F11.5,1X,' SCALE FACTOR: POP OUT = REAL POP * SCFAC')
9510 FORMAT(1X,'E-STATE ',A3)
9515 FORMAT(1X,'BRANCH ',A1)
9520 FORMAT(5X,'V=',5(I4,5X),(:/9X,5(I4,5X)))
9525 FORMAT(1X,'J=',I2,2X,5F9.4,(:/9X,5F9.4))
9530 FORMAT(1X,'SUM ',5F9.4,(:/9X,5F9.4))
9535 FORMAT(1X,'FRAC ',5F9.4,(:/9X,5F9.4))
9540 FORMAT(1X,'ERRORS')
9545 FORMAT(1X,'SUM FOR BRANCH',F12.3,' +/-',F12.3/)
9996 FORMAT(1X,'ERROR ENCOUNTERED WHEN SORTING TRANSITION LIBRARY(.'/1X,
1'ENTRY ',I4,4X,F7.2,'CM-1',I3,A1,I2,2X,F3.1,A1,' AND'/1X,
2'ENTRY ',I4,4X,F7.2,'CM-1',I3,A1,I2,2X,F3.1,A1,' APPEAR TO BE',1X,
3'IDENTICAL STATES')

```

C
C
C

DATA INITIALISED AND PARAMETERS DETERMINED

```

READ(2,1010) DATE
WRITE(7,1015) DATE
WRITE(6,1015) DATE
READ(2,1020) PNM
NDPTS=16334.
RSL=1./(NDPTS*0.5325E-4)
PSCL=3949.5/NDPTS
READ(2,1040) NLCULE
READ(2,1020) TRSITP
WRITE(7,1045) NLCULE,PNM,TRSITP
WRITE(6,1045) NLCULE,PNM,TRSITP
READ(2,1050) WMIN,WMAX
WRITE(7,1055) WMIN,WMAX
WRITE(6,1055) WMIN,WMAX
IPT5=INT(WMIN/PSCL)
IPT2=INT(WMAX/PSCL)
NPTS=IPT2-IPT5+1
NFE=2
RDVAL=0
DO 106 L=1,4
DO 107 K=1,3
POP3(K,L)=0.0
POPBE(K,L)=0.0

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DO 103 J=1,10
POPV(J,K,L)=0.0
POPVE(J,K,L)=0.0
PVMX(J,K,L)=0.0
DO 109 I=0,50
POPL(I,J,K,L)=0.0
POPLE(I,J,K,L)=0.0
SORT(I,J,K,L)=0
109 CONTINUE
108 CONTINUE
107 CONTINUE
106 CONTINUE
150 DO 105 I=1,3
VMIN(I)=10
VMAX(I)=0
JBMX(I)=0
JBMN(I)=50
105 CONTINUE
NN=0
WRITE(6,1070)
WRITE(7,1075)
PFLAG=0
QFLAG=0
RFLAG=0
120 NN=NN+1
READ(NFR,1030) VVLU(NN),SRV(NN),JLNN(NN),JENN(NN)
IF (SRV(NN).EQ.'P') PFLAG=1
IF (SRV(NN).EQ.'Q') QFLAG=1
IF (SRV(NN).EQ.'R') RFLAG=1
IF (SRV(NN).EQ.'D') GO TO 110
NV=VVLU(NN)
CALL INTVAL(1.5,SRV(NN),'+',N2,N3)
IF (VVLU(NN).GT.VMAX(N3)) VMAX(N3)=VVLU(NN)
IF (VVLU(NN).LT.VMIN(N3)) VMIN(N3)=VVLU(NN)
IF (JENN(NN).GT.JBMX(N3)) JBMX(N3)=JENN(NN)
IF (JLNN(NN).LT.JBMN(N3)) JBMN(N3)=JLNN(NN)
GO TO 120
110 NA=NN-1
DO 130 I=1,NA
WRITE(7,1090) VVLU(I),SRV(I),JLNN(I),JENN(I)
WRITE(6,1090) VVLU(I),SRV(I),JLNN(I),JENN(I)
130 CONTINUE
WRITE(6,1100)
WRITE(7,1100)
READ(5,1000) ANS
WRITE(7,1000) ANS
IF (ANS.EQ.'Y') GO TO 140
NFR=0
GO TO 150
140 NFA=2

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C
C THE SPECTRUM TO BE ANALYZED IS READ IN
C NCAD=THE NUMBER OF INTERFEROGRAM FILES THAT WERE ADDED
C SCNS=THE TOTAL NUMBER OF COMPLETE SCANS REPRESENTED BY THIS SPECTRUM
C RDVD=___ IF = "RDV" THEN THE SPECTRUM HAS BEEN CORRECTED FOR LASER
C SPIKES AND INTERFEROMETER RESPONSE
C IF = ANYTHING ELSE THE SPECTRUM WILL BE CORRECTED FOR
C THE INTERFEROGRAM RESPONSE, YOU WILL HAVE THE
C OPTION TO REMOVE LASER SPIKES (ALL LASER SPIKES
C BETWEEN 2000 AND 3950 CM-1 SHOULD BE REMOVED THIS
C FIRST TIME). THEY CANNOT BE PREDEFINED IN THE PROGRA
C SINCE THEIR SHAPE CHANGES FROM ONE FILE TO THE
C NEXT AND SOME LINES ARE ON THE WINGS. SUGGESTED
C RANGES AND THEIR OVERLAPPED SPECTRAL LINES ARE:
C 2630.0 TO 2638.0 (HCL 2P7 AND 3P2)
C 3100.0 TO 3106.0 (OH 3P3 1/2) -SMALL INTENSITY
C 3362.0 TO 3366.0 (OH 1P4 3/2) -SMALL INTENSITY
C 3379.0 TO 3593.0 (HF 1P3, 2P5, AND 3P1)
C THE CORRECTED SPECTRUM IS WRITTEN TO A NEW FILE FOR FUTURE USE
C ALONG WITH THE AVERAGE VALUE OF THE UNCORRECTED SPECTRUM BETWEEN
C 2000 AND 3950 CM-1.
C
C IF (RDVAL.GT.0) GO TO 405
C RDVAL=1
C READ(3,2005) NCAD
C READ(3,2010) SCNS,RDVD,AVRG
C READ(3,2020) (PTS(I),I=1,16364)
C READ(3,2020) (RDV(I),I=1,16364)
C SECTION CHANGED TO READ IN VALUES FROM .FHT BINARY FILES ON UNIT 3
C OPEN (3, ACCESS='DIRECT', RECORDTYPE='FIXED', RECL=123,
1 STATUS='OLD', READONLY, FORM='UNFORMATTED',
2 CARRIAGECONTROL='NONE' )
C OPEN (3, ACCESS='DIRECT', RECORDTYPE='FIXED', RECL=123,
1 STATUS='OLD', READONLY, FORM='UNFORMATTED',
2 CARRIAGECONTROL='NONE' )
C DO 243 J = 1, 64
C READ(3,J,ERR=244,IOSTAT=IOS) (I2(I), I=1, 256)
C READ(3,J,ERR=244,IOSTAT=IOS) (I2RDV(I), I=1, 256)
C GO TO 245
C 243 WRITE(6,*) 'EOF ON .FHT FILE, RECORD J=',J
C GO TO 243
C 244 WRITE(6,*) 'ERR ON .FHT FILE, RECORD, ERROR = ',J,IOS
C GO TO 243
C 245 IF (J.GT.1) GO TO 246
C NCAD = I2(14)
C SCNS = 3 * NCAD
C AVRG = 0.0
C GO TO 243
C 246 DO 247 I = 1, 256
C PTS ( (J-1)*256 + I ) = 2*PTI2 ( I2(I) ) * 100.0
C 247 RDV((J-1)*256+I)=2*PTI2(I2RDV(I))
C 245 CONTINUE

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      RDVD = 'XXX'
      IF (RDVD.EQ.'RDV') GO TO 210
      WRITE(6,2030)
      READ(2,1000) ANS
      WRITE(7,1000) ANS
      IF (ANS.NE.'Y') GO TO 220
250  WRITE(6,2040)
      READ(2,2050) NSLG,(SLG(I),I=1,10)
      WRITE(7,2055) NSLG,(SLG(I),I=1,2*NSLG)
      WRITE(6,2055) NSLG,(SLG(I),I=1,2*NSLG)
      DO 230 I=1,NSLG*2,2
      XPS=SLG(I)/PSCL
      XPE=SLG(I+1)/PSCL
      IXPS=INT(XPS)-1
      IXPE=INT(XPE)+1
      VMD=(PTS(IXPS)+PTS(IXPE))/2.0
      DO 240 J=IXPS,IXPE
      PTS(J)=VMD
240  CONTINUE
230  CONTINUE
      WRITE(6,2060) NSLG
      READ(5,1000) ANS
      IF (ANS.EQ.'Y') THEN
      NPT=0
      GO TO 250
      END IF
220  AVRG=0.0
      IEPT=1PT*25
      IF (IEPT.GT.16384) THEN
      IEPT=16384
      PTSCNT=PTS(16384)/RDV(16384)
      DO 255 I=1,10
      IAD=16384+I
      PTS(IAD)=PTSCNT
255  CONTINUE
      END IF
      DO 260 I=1PTS-25,IEPT
      AVRG=AVRG+PTS(I)
      PTS(I)=PTS(I)/RDV(I)
260  CONTINUE
      AVRG=AVRG/REAL(NPTS)
C      WRITE(9,2005) NCAD
C      WRITE(9,2010) SCNS,RDVM,AVRG
C      WRITE(9,2020) (PTS(I),I=1,16384)
210  CONTINUE
      WRITE(7,2071) AVRG
C      WRITE(7,2070) NCAD,SCNS,AVRG
C
C      FIND MAXIMUM AND MINIMUM IN SPECTRAL REGION TO BE ASSIGNED
C

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MAXI=0.0
MINI=100.0
MAXPT=8295
MINPT=16384
AVRS=0.0
WRITE(6,211)
211  FORMAT(1X,'INPUT SMOOTHING PARAMETER. (0,1,2, OR 3)')
      READ(5,3000) ISMOOT
      CALL SMOOTH(IPTS,IPTZ,ISMOOT)
      DO 310 I=IPTS,IPTZ
        AVRS=AVRS+PTS(I)
        IF (PTS(I).LT.MAXI) GO TO 320
        MAXI=PTS(I)
        MAXPT=I
320   IF (PTS(I).GT.MINI) GO TO 310
        MINI=PTS(I)
        MINPT=I
310   CONTINUE
      AVRS=AVRS/REAL(NPTS)
      WNMAT=REAL(MAXPT)*PSCL
      WNMAT=REAL(MINPT)*PSCL
      YMEDV=MINI*RDV(MINPT)
      MAXL=MAXI-MINI
      WRITE(7,3010) MINI,WNMAT,MAXL,WNMAT

C
C   TRANSITION LIBRARY IS SEARCHED AND ANY LINE WITHIN THE (V LEVEL,
C   BRANCH,J LEVEL) SPECIFICATIONS GIVEN IS STORED IN A CATALOGUE.
C   NOTE, LINES ARE NOT ASSIGNED IF THEY LIE OUTSIDE THE SPECTRAL
C   WINDOW INDICATED.
C   THE TRANSITION THAT LIES WITHIN THE INSTRUMENTAL RESOLUTION (RSL)
C   OF THE MAXIMUM INTENSITY IS ASSIGNED TO BE THE MAXIMUM LINE.
C
405  N=1
      NMAX=0
      DO 410 I=1,1444
        READ(4,4010,END=406)
          1      FREQ(N),BR(N),AFAC(N),VUP(N),JLST(N),EST(N),PTY(N)
C          IF (I.LE.5) WRITE (6,4010)
C          1      FREQ(N),BR(N),AFAC(N),VUP(N),JLST(N),EST(N),PTY(N)
        GO TO 409
406  WRITE (6,*) 'EOP UNIT 4: I,N=',I,N
409  CONTINUE
      JLOW(N)=INT(JLST(N)-EST(N))
      DO 420 J=1,NA
        IF (BR(N).NE.BRV(J)) GO TO 420
        IF (VUP(N).NE.VVLU(J)) GO TO 420
        IF (JLOW(N).LT.JLNN(J)) GO TO 430
        IF (JLOW(N).GT.JHNN(J)) GO TO 430
        IF (ABS(FREQ(N)-JNMAX).LT.RSL) NMAX=N
        IF (FREQ(N).GE.WMIN.AND.FREQ(N).LE.WMAX) GO TO 415
        WRITE(7,4020) VUP(N),BR(N),JLOW(N),EST(N),PTY(N),FREQ(N)

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      IF (PREQ(N).LT.WMIN) THEN
        IF (JLOW(N).EQ.JLNN(J)) JLNN(J)=JLNN(J)+1
        IF (JLOW(N).EQ.JHNN(J)) JHNN(J)=JHNN(J)-1
      ELSE
        IF (BR(N).EQ.'R') JHNN(J)=JLOW(N)-1
        IF (BR(N).NE.'R') JLNN(J)=JLOW(N)+1
      END IF
      IF (JHNN(J).LT.0.OR.JLNN(J).GT.50) THEN
        WRITE(6,4025) VVLU(J),BRV(J)
        WRITE(7,4025) VVLU(J),BRV(J)
        GO TO 150
      END IF
      GO TO 410
415    DO 440 II=1,6
        OVL(II,N)=1
440    CONTINUE
        N=N+1
        GO TO 430
420    CONTINUE
430    CONTINUE
410    CONTINUE

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      NLST=N-1
      WRITE(7,4030) NLST
      WRITE(7,4040)
      WRITE(5,4040)
      DO 450 I=1,NA
        NV=VVLU(I)
        CALL INTVAL(1.5,BRV(I),'+',NE,NB)
        ASSGN(1,NV,NB)=JLNN(I)
        ASSGN(2,NV,NB)=JHNN(I)
        WRITE(7,4050) VVLU(I),BRV(I),JLNN(I),JHNN(I)
        WRITE(6,4050) VVLU(I),BRV(I),JLNN(I),JHNN(I)
450    CONTINUE

```

C
C VERIFY IDENTITY OF MAXIMUM LINE. IF INCORRECT, NEW MAXIMUM LINE
C IS QUERIED AND FOUND IN THE CATALOGUE. THIS IS NOT TERRIBLY
C IMPORTANT SINCE THE RESULTS ARE NOT SCALED TO THE MAXIMUM.
C

```

      IF (NMAX.NE.0) GO TO 510
      WRITE(5,5010) RSL,NMAX
      WRITE(7,5010) RSL,NMAX
      GO TO 520
510    VUPX=VUP(NMAX)
      BRX=BR(NMAX)
      JLOWX=JLOW(NMAX)
      ESTX=EST(NMAX)
      PRTYX=PTY(NMAX)
      WRITE(5,5020) VUP(NMAX),BR(NMAX),JLOW(NMAX),EST(NMAX),PTY(NMAX)
      WRITE(7,5020) VUP(NMAX),BR(NMAX),JLOW(NMAX),EST(NMAX),PTY(NMAX)
      READ(5,1000) ANS
      WRITE(7,1000) ANS
      IF (ANS.EQ.'Y') GO TO 530

```

```

520 WRITE(6,5030)
    WRITE(7,5030)
    READ(5,5040) VUPX,BRX,JLOWX,ESTX,PRTYX
    WRITE(7,5040) VUPX,BRX,JLOWX,ESTX,PRTYX
    CALL MAXID(VUPX,BRX,JLOWX,ESTX,PRTYX,NMAX)

```

```

530 CONTINUE

```

```

C
C THE CATALOGUE IS SORTED AND OVERLAPS IDENTIFIED. AN ARRAY IS
C SET UP IN WHICH THE FIRST SUBSCRIPT IS THE VALUE OF J-LOWER, THE
C SECOND SUBSCRIPT IS THE VALUE OF V-UPPER, THE THIRD SUBSCRIPT IS
C INDICATIVE OF THE BRANCH (P=1, Q=2, AND R=3), AND THE FOURTH
C SUBSCRIPT IS DETERMINED BY THE E-STATE AND PARITY
C ( $3/2+=1$ ,  $3/2-=2$ ,  $1/2+=3$ , AND  $1/2-=4$ ).
C THE ARRAY ELEMENT IS GIVEN THE VALUE OF THE SUBSCRIPT OF THE
C LINE IN THE CATALOGUE. IE FOR THE N*TH LINE IN THE CATALOGUE,
C  $SORT(JLOW(N),VUP(N),BR(N),EST/PRTY(N))=N$ .
C
C OVERLAPS (WHEN LINES ARE WITHIN 2*(THE INSTRUMENTAL RESOLUTION) OF
C EACH OTHER) ARE KEPT TRACK OF BY AN OVERLAP ARRAY OVL(I,N) FOR
C EACH LINE IN THE CATALOGUE. THE SECOND SUBSCRIPT, N, IS THE
C SUBSCRIPT OF THE LINE IN THE CATALOGUE. THE FIRST SUBSCRIPT,
C I, IS OF DIMENSIONALITY 6. IT'S FIRST ENTRY INDICATES THE NUMBER
C OF LINES THAT ARE OVERLAPPED WITH LINE N - FOR NO OVERLAPS IT HAS
C THE VALUE 1, IF OVERLAPPED WITH (J-1) OTHER LINES IT HAS THE
C VALUE J, AND IF THE LINE HAS BEEN AVERAGED INTO THE LINE THAT IS
C THE SAME STATE BUT DIFFERENT PARITY IT HAS THE VALUE 0. SUBSEQUENT
C ENTRIES ARE THE SUBSCRIPTS OF THE OVERLAPPED LINES IN THE CATALOGUE.
C IE FOR LINE 13 OVERLAPPED WITH LINES 14, AND 16:
C
C     OVL(1,13)=3
C     OVL(2,13)=14
C     OVL(3,13)=16
C     OVL(4,13)=0
C     OVL(5,13)=0
C     OVL(6,13)=0
C
C     OVFLAG=0
C     DO 610 I=1,NLST
C       IF (FREQ(I).EQ.0.0) GO TO 630
C       J=I+1
560 IF (J.GT.NLST) GO TO 640
C       IF (FREQ(J).EQ.0.0) GO TO 655
C       IF (ABS(FREQ(I)-FREQ(J)).GT.RSL) GO TO 640
C       IF (BR(I).NE.BR(J)) GO TO 650
C       IF (VUP(I).NE.VUP(J)) GO TO 650
C       IF (JLOW(I).NE.JLOW(J)) GO TO 650
C       IF (EST(I).NE.EST(J)) GO TO 650
C       IF (PRTY(I).EQ.PRTY(J)) GO TO 630
C       FREQ(I)=0.5*(FREQ(I)+FREQ(J))
C       AFAC(I)=0.5*(AFAC(I)+AFAC(J))
C       FREQ(J)=0.0
C       NV=VUP(J)
C       NJ=JLOW(J)

```

```

      CALL INTVAL(EST(J),BR(J),PRTY(J),NE,NB)
      SORT(NJ,NV,NB,NE)=J
      IF (OVL(1,J).EQ.1) GO TO 652
      K=OVL(1,J)
      DO 651 IK=2,K
      KL=OVL(IK,J)
      KP=OVL(1,KL)
      DO 653 IKP=2,KP
      IF (OVL(IKP,KL).NE.J) GO TO 653
      OVL(1,KL)=OVL(1,KL)-1
      KST=IKP+1
      DO 654 KSPT=KST,6
      OVL(KSPT-1,KL)=OVL(KSPT,KL)
654 CONTINUE
      OVL(6,KL)=1
      GO TO 651
653 CONTINUE
651 CONTINUE
652 CONTINUE
      OVL(1,J)=0
      IF (J.EQ.NMAX) NMAX=I
      GO TO 655
650 OVL(1,I)=OVL(1,I)+1
      N=OVL(1,I)
      OVL(N,I)=J
      OVL(1,J)=OVL(1,J)+1
      N=OVL(1,J)
      OVL(N,J)=I
      OVFLAG=OVFLAG+1
655 J=J+1
      GO TO 660
640 NV=VUP(I)
      NJ=JLOW(I)
      CALL INTVAL(EST(I),BR(I),PRTY(I),NE,NB)
      SORT(NJ,NV,NB,NE)=I
630 FC(I)=1.0
610 CONTINUE
      IF (OVFLAG.NE.0) THEN
      WRITE(7,6010)
      WRITE(6,6010)
      WRITE(7,6020)
      WRITE(6,6020)
      DO 670 I=1,NLST
      IF (OVL(1,I).GT.1) THEN
      WRITE(7,6030) I,VUP(I),BR(I),JLOW(I),EST(I),PRTY(I),
      1(OVL(1,I),J=1,6)
      WRITE(6,6030) I,VUP(I),BR(I),JLOW(I),EST(I),PRTY(I),
      1(OVL(1,I),J=1,6)
      END IF
670 CONTINUE

```

```

ELSE
WRITE(7,6040)
WRITE(6,6040)
END IF
WRITE(6,6050)
WRITE(7,6050)
NBS=1
NBP=1
NBI=1
IF (PFLAG.EQ.0) NBS=2
IF (QFLAG.EQ.1) THEN
NBP=2
ELSE
IF (PFLAG.EQ.0) THEN
NBS=3
ELSE
NBI=2
END IF
END IF
IF (RFLAG.EQ.1) NBP=3
JMX=1LX0(JBMX(1),JBMX(2),JBMX(3))
DO 690 L=1,4
DO 691 K=NBS,NBP,NBI
VMN=VMIN(K)
VMX=VMAX(K)
DO 692 J=VMN,VMX
WRITE(7,6050) EPLBL(L),BLBL(K),J,(SORT(I,J,K,L),I=0,JMX)
WRITE(6,6060) EPLBL(L),BLBL(K),J,(SORT(I,J,K,L),I=0,JMX)
692 CONTINUE
691 CONTINUE
690 CONTINUE

```

C
C MAXIMUM LINE TESTED FOR OVERLAPS, AND IT IS HANDLED IF REQUIRED.
C

```

740 IF (OVL(1,NMAX).LE.1) GO TO 710
NUM=OVL(1,NMAX)-1
N=NMAX
WRITE(6,7010) VUP(N),BR(N),JLOW(N),EST(N),PRTY(N),NUM
WRITE(7,7010) VUP(N),BR(N),JLOW(N),EST(N),PRTY(N),NUM
DO 720 I=1,NUM
J=I+1
K=OVL(J,N)
WRITE(6,7020) VUP(K),BR(K),JLOW(K),EST(K),PRTY(K)
WRITE(7,7020) VUP(K),BR(K),JLOW(K),EST(K),PRTY(K)
720 CONTINUE
WRITE(6,7030)
WRITE(7,7030)
READ(5,1000) ANS
WRITE(7,1005) ANS
IF (ANS.EQ.'Y') GO TO 710

```



```

WRITE(6,7040)
WRITE(7,7040)
READ(5,7020) VUPX,BRX,JLOWX,ESTX,PRTYX
WRITE(7,7025) VUPX,BRX,JLOWX,ESTX,PRTYX
750 CALL MAXID(VUPX,BRX,JLOWX,ESTX,PRTYX,NMAX)
GO TO 740
710 IF(FREQ(NMAX).NE.0.0) GO TO 730
IF (PRTYX.EQ.'+') THEN
PRTYX='-'
ELSE
PRTYX='+'
END IF
WRITE(6,7050)
WRITE(7,7050)
GO TO 750
730 WRITE(6,7060) VUPX,BRX,JLOWX,ESTX,PRTYX
WRITE(7,7060) VUPX,BRX,JLOWX,ESTX,PRTYX
C
C IF ANY LINES NEED ADJUSTING FOR ABSORPTION ETC IT CAN BE DONE
C THE HEIGHT OF THE LINE FROM THE 'LOCAL' MINIMUM IS MULTIPLIED
C BY THE VALUE SUPPLIED.
C
WRITE(6,8010)
READ(5,1000) ANS
IF (ANS.EQ.'N') GO TO 310
WRITE(6,8020)
WRITE(7,8025)
820 READ(5,3030) VUPX,BRX,JLOWX,ESTX,PRTYX,PAC
IF (BRX.EQ.'D') GO TO 510
WRITE(7,3040) VUPX,BRX,JLOWX,ESTX,PRTYX,PAC
CALL INTVAL(ESTX,BRX,PRTYX,N2,NB)
LN=SORT(JLOWX,VUPX,N3,N2)
CALL SWITCH(JLOWX,VUPX,N3,NE,NR2,LN,LR)
LRN=SORT(JLOWX,VUPX,N3,NR2)
FC(LN)=PAC
FC(LRN)=PAC
GO TO 320
810 CONTINUE
C
C CALCULATION OF POPULATIONS AND OUTPUT
C
PMAX=0.0
WRITE(7,9005)
DO 910 IN=1,NLST
ZI=EST(IN)
CB=BR(IN)
CP=PRTY(IN)
IV=VUP(IN)
IJ=JLOW(IN)
WIN=FREQ(IN)
AFIN=AFAC(IN)

```

```

CALL INTVAL(ZI,CS,CP,NZ,NB)
CALL SWITCH(IJ,IV,NB,NE,NF,IN,ID)
IF (WIN.EQ.0.0) THEN
CALL XVALUE(ID,IPTY,YP)
CALL LOCAL(IPTY,YMNL,YAVL,YMXL,IPYMXL)
IF (OVL(1,ID).LT.0) PTS(IPTY)=YASGN(ID)
YVLU=(PTS(IPTY)-YMNL)*FC(IN)
GO TO 920
END IF
IF (OVL(1,IN)-1) 925,930,935
935 WRITE(6,9001) IN,IV,CS,IJ,ZI,CP,WIN
WRITE(7,9001) IN,IV,CS,IJ,ZI,CP,WIN
CALL OVRLP(IN,YASGN)
925 IPTY=NINT(WIN/PSCL)
PTS(IPTY)=YASGN(IN)
GO TO 940
930 CALL XVALUE(IN,IPTY,YP)
940 CALL LOCAL(IPTY,YMNL,YAVL,YMXL,IPYMXL)
POPLE(IJ,IV,NB,NE)=(YAVL-YMNL)/(AFIN*WIN)
YVLU=(PTS(IPTY)-YMNL)*FC(IN)
POPL(IJ,IV,NB,NZ)=YVLU/(AFIN*WIN)-POPLE(IJ,IV,NB,NE)
IF (FC(IN).EQ.0.0) THEN
POPL(IJ,IV,NB,NE)=0.0
POPLE(IJ,IV,NB,NE)=0.0
END IF
920 PLEP=(POPL(IJ,IV,NB,NE)+POPL(IJ,IV,NB,NF))/2.0
PLEPE=(POPLE(IJ,IV,NB,NE)+POPLE(IJ,IV,NB,NF))/2.0
IF (POPL(IJ,IV,NB,NE).EQ.0.0) THEN
PLEP=POPL(IJ,IV,NB,NF)
PLEPE=POPLE(IJ,IV,NB,NF)
END IF
IF (POPL(IJ,IV,NB,NF).EQ.0.0) THEN
PLEP=POPL(IJ,IV,NB,NE)
PLEPE=POPLE(IJ,IV,NB,NE)
END IF
POPL(IJ,IV,NB,NE)=PLEP
POPLE(IJ,IV,NB,NE)=PLEPE
IF (POPL(IJ,IV,NB,NE).LT.POPLE(IJ,IV,NB,NE))
1 POPL(IJ,IV,NB,NE)=-POPLE(IJ,IV,NB,NE)
WRITE(7,9007) IN,IV,CS,IJ,ZI,CP,WIN,IPTY,PTS(IPTY),YMNL,FC(IN),
1YVLU,AFIN,POPL(IJ,IV,NB,NE),POPLE(IJ,IV,NB,NE)
WRITE(5,9007) IN,IV,CS,IJ,ZI,CP,WIN,IPTY,PTS(IPTY),YMNL,FC(IN),
1YVLU,AFIN,POPL(IJ,IV,NB,NE),POPLE(IJ,IV,NB,NE)
POPV(IV,NB,NE)=POPV(IV,NB,NE)+ABS(POPL(IJ,IV,NB,NE))
POPVE(IV,NB,NE)=POPVE(IV,NB,NE)+POPLE(IJ,IV,NB,NE)**2
IF (ABS(POPL(IJ,IV,NB,NE)).GT.PVMX(IV,NB,NE)) THEN
PVMX(IV,NB,NE)=ABS(POPL(IJ,IV,NB,NE))
END IF
IF (ABS(POPL(IJ,IV,NB,NE)).GT.PMAX) PMAX=ABS(POPL(IJ,IV,NB,NE))
POPd(NB,NE)=POPd(NB,NE)+ABS(POPL(IJ,IV,NB,NE))
POPBE(NB,NE)=POPBE(NB,NE)+POPLE(IJ,IV,NB,NE)**2
910 CONTINUE

```

```

      SCFAC=1.0
311 IF (PMAX.GT.1.0) GO TO 912
      PMAX=PMAX*10.0
      SCFAC=SCFAC*10.0
      GO TO 911
312 IF (PMAX.LT.10.0) GO TO 913
      PMAX=PMAX/10.0
      SCFAC=SCFAC/10.0
      GO TO 912
313 WRITE(6,*) 'WHEN READY FOR OUTPUT PRESS <CR>'
      READ (5,*)
      WRITE(7,9009)
      DO 945 NE=1,4,2
      WRITE(7,9010) ELBL(NZ)
      WRITE(6,9010) ELBL(NZ)
      DO 950 NB=NBS,NBF,NBI
      POPBE(NB,NE)=SQRT(POPBE(NB,NE))
      NVS=VMIN(NB)
      NVE=VMAX(NB)
      JND=JBMX(NB)
      JST=JBMN(NB)
      DO 960 I=NVS,NVE
      POPVE(I,NB,NE)=SQRT(POPVE(I,NB,NE))
960 CONTINUE
330 WRITE(7,9020) BLBL(NB)
      WRITE(6,9020) BLBL(NB)
      WRITE(7,9030) (JLBL(I),I=JST,JND)
      DO 955 NV=NVS,NVZ
      IF (PVMX(NV,NB,NE).GE.100.0) SCAL=0.01
      IF (PVMX(NV,NB,NE).LT.100.0.AND.PVMX(NV,NB,NE).GE.10.0)
1      SCAL=0.1
      IF (PVMX(NV,NB,NE).LT.10.0.AND.PVMX(NV,NB,NE).GE.1.0)
1      SCAL=1.0
      IF (PVMX(NV,NB,NE).LT.1.0.AND.PVMX(NV,NB,NE).GE.0.1)
1      SCAL=10.0
      IF (PVMX(NV,NB,NE).LT.0.1.AND.PVMX(NV,NB,NE).GE.0.01)
1      SCAL=100.0
      IF (PVMX(NV,NB,NE).LT.0.01.AND.PVMX(NV,NB,NE).GE.0.001)
1      SCAL=1000.0
      IF (PVMX(NV,NB,NE).LT.0.001) SCAL=10000.0
      WRITE(7,9046) SCAL,SCAL
      WRITE(7,9047) NV,(SCAL*POPPL(NJ,NV,NB,NE),
1      SCAL*POPPL(NJ,NV,NB,NE),NJ=JST,JND)
955 CONTINUE
      WRITE(7,9050)
      DO 965 I=NVS,NVE
      PVFR=POPV(I,NJ,NZ)/POPJ(NB,NZ)
      PVFRZ=POPVE(I,NB,NE)/POPB(NB,NE)
      WRITE(7,9060) I,SCAL*POPV(I,NB,NE),SCAL*POPVE(I,NB,NE),PVFR,PVFRZ
965 CONTINUE
      WRITE(7,9070) SCAL*POPJ(NB,NZ),SCAL*POPB(NB,NE)
      WRITE(6,9070) SCFAC
      WRITE(6,9080) (VLBL(I),I=NVS,NVE)

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```

DO 970 NJ=JST,JND
WRITE(6,9090) NJ,(SCFAC*POPL(NJ,I,NB,NE),I=NVS,NVE)
970 CONTINUE
WRITE(6,9100) (SCFAC*POPV(I,NB,NE),I=NVS,NVE)
WRITE(6,9105) (SCFAC*POPVE(I,NB,NE),I=NVS,NVE)
WRITE(6,9110)
READ(5,1000) ANS
IF (ANS.NE.'Y') GO TO 950
WRITE(6,9120)
WRITE(7,9125)
985 READ(5,9130) VX,BX,JX,PNEW
PNEW=PNEW/SCFAC
WRITE(7,9140) VX,BX,JX,PNEW
IF (BX.EQ.'D') GO TO 930
CALL INTVAL(1.5,BX,'+',NEX,NBX)
IF (NBX.NE.NB.OR.VX.LT.NVS.OR.VX.GT.NVE.OR.JX.LT.JST.OR.JX.GT.JND
1) THEN
WRITE(6,9135)
GO TO 935
END IF
POPB(NB,NE)=POPB(NB,NE)-ABS(POPL(JX,VX,NB,NE))+PNEW
POPV(VX,NB,NE)=POPV(VX,NB,NE)-ABS(POPL(JX,VX,NB,NE))+PNEW
POPL(JX,VX,NB,NE)=-PNEW
IF (ABS(PNEW).GT.PVMX(JX,NB,NE)) P/MX(JX,NB,NE)=ABS(PNEW)
GO TO 985
950 CONTINUE
WRITE(6,*) 'WHEN READY FOR OUTPUT PRESS <CR>'
READ(5,*)
945 CONTINUE
WRITE(10,9500) DATE,FNM,MLCULE
WRITE(10,9501) ISMOOT
WRITE(10,9502) NBS,NBF,NBI
WRITE(10,9503) (VMIN(I),I=1,3)
WRITE(10,9504) (VMAX(I),I=1,3)
WRITE(10,9505) (JBMN(I),I=1,3)
WRITE(10,9506) (JBMX(I),I=1,3)
WRITE(10,9507) SCFAC
DO 990 NE=1,3,2
WRITE(10,9510) ELBL(NE)
WRITE(6,9510) ZLBL(NE)
DO 995 NB=NBS,NBF,NBI
WRITE(10,9515) BLBL(NB)
WRITE(6,9515) BLBL(NB)
WRITE(6,9550)
NVS=VMIN(NB)
NVE=VMAX(NB)
NJS=JBMN(NB)
NJE=JBMX(NB)
NEV=5
IF (NVE.GT.5) NEV=10

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```

DO 989 I=NVS,NVZ
PVPR=POPV(I,NB,NZ)/POPB(NB,NZ)
PVPZ=POPVZ(I,NB,NZ)/POPB(NB,NZ)
WRITE(6,9060) I,SCFAC*POPV(I,NB,NZ),SCFAC*POPVZ(I,NB,NZ),PVPR,
1 PVPZ
958 CONTINUE
WRITE(6,9070) SCFAC*POPB(NB,NZ),SCFAC*POPBZ(NB,NZ)
WRITE(10,9520) (VLBL(I),I=1,NEV)
DO 997 NJ=NJS,NJZ
WRITE(10,9525) NJ,(SCFAC*POPL(NJ,NV,NB,NZ),NV=1,NEV)
997 CONTINUE
WRITE(10,9530) (SCFAC*POPV(NV,NB,NZ),NV=1,NEV)
WRITE(10,9535) (POPV(NV,NB,NZ)/POPB(NB,NZ),NV=1,NEV)
WRITE(10,9540)
WRITE(10,9520) (VLBL(I),I=1,NEV)
DO 999 NJ=NJS,NJZ
WRITE(10,9525) NJ,(SCFAC*POPL(NJ,NV,NB,NZ),NV=1,NEV)
999 CONTINUE
WRITE(10,9530) (SCFAC*POPVZ(NV,NB,NZ),NV=1,NEV)
WRITE(10,9535) (POPVZ(NV,NB,NZ)/POPB(NB,NZ),NV=1,NEV)
WRITE(10,9545) SCFAC*POPB(NB,NZ),SCFAC*POPBZ(NB,NZ)
995 CONTINUE
990 CONTINUE
GO TO 9900
9993 WRITE(6,9993) I,PRZQ(I),VUP(I),BR(I),JLOW(I),EST(I),PTY(I),J,
1FREQ(J),VUP(J),BR(J),JLOW(J),EST(J),PTY(J)
9900 STOP
END
C *****SMOOTH*****
SUBROUTINE SMOOTH(IPTS,IPTZ,ISMOT)
DIMENSION PTS(16400),R(25)
COMMON/116K/ AVRS,YMRDV,PTS,KDV
JS=IPTS-10
JZ=IPTZ+10
GO TO (100,200,300) ISMOT
WRITE(6,*) 'DATA NOT SMOOTHED'
WRITE(7,*) 'DATA NOT SMOOTHED'
RETURN
100 DO 110 I=2,5
110 R(I)=PTS(JS+I-2)
DO 130 I=JS+2,JZ-2
DO 120 K=1,4
120 R(K)=R(K+1)
R(5)=PTS(I+2)
RSUM=17.*R(3)+12.*(R(4)+R(2))- 3.*(R(1)+R(5))
130 PTS(I)=RSUM/35.0
WRITE(6,*) '5 PT DATA SMOOTH COMPLETE'
WRITE(7,*) '5 PT DATA SMOOTH COMPLETE'
RETURN
200 DO 210 I=2,5
210 R(I)=PTS(JS+I-2)

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DO 230 I=JS+4,JZ-4
DO 220 K=1,8
220 R(K)=R(K+1)
R(9)=PTS(I+4)
RSUM=59.*R(5)+54.*(R(4)+R(6))+39.*(R(3)+R(7))+14.*(R(2)+R(8))-
1 21.*(R(1)+R(9))
230 PTS(I)=RSUM/231.0
WRITE(6,*) '9 PT DATA SMOOTH COMPLETE'
WRITE(7,*) '9 PT DATA SMOOTH COMPLETE'
RETURN
300 DO 310 I=2,17
310 R(I)=PTS(JS+I-2)
DO 330 I=JS+8,JE-8
DO 320 K=1,16
320 R(K)=R(K+1)
R(17)=PTS(I+8)
RSUM=43.*R(9)+42.*(R(8)+R(10))+39.*(R(7)+R(11))
1 +34.*(R(6)+R(12))+27.*(R(5)+R(13))
2 +15.*(R(4)+R(14))+ 7.*(R(3)+R(15))
3 - 6.*(R(2)+R(16))-21.*(R(1)+R(17))
330 PTS(I)=RSUM/323.0
WRITE(6,*) '17 PT DATA SMOOTH COMPLETE'
WRITE(7,*) '17 PT DATA SMOOTH COMPLETE'
RETURN
END
C *****INTVAL*****
SUBROUTINE INTVAL(ZST,BR,PTY,NZ,NB)
CHARACTER*1 BR,PTY
NE=1
IF (ZST.EQ.0.5) NZ=3
NP=0
IF (PTY.EQ.'-') NP=1
NZ=NE+NP
NB=1
IF (BR.EQ.'Q') NB=2
IF (BR.EQ.'R') NB=3
RETURN
END
C *****MAXID*****
SUBROUTINE MAXID(VUPX,BRX,JLOWX,ESTX,PTYX,NMAX)
CHARACTER*1 ANS,BR,BRV,BRX,PTY,PTYX
INTEGER*4 VUPX,VUP
DIMENSION BR(1450),VUP(1450),JLOW(1450),EST(1450),PTY(1450)
COMMON/N1450/ NLST,VUP,JLOW,EST
COMMON/CHARS/ BR,PTY
1100 FORMAT(///1X,'THIS LINE IS NOT IN THE CATALOGUE.')
1200 FORMAT(1X,'CHOOSE A LINE FROM THE FOLLOWING:')
1300 FORMAT(I2,A1,I2,1X,F3.1,A1)
1400 FORMAT(1X,'INPUT MAXIMUM LINE: V(UPPER)-BRANCH-J(UPPER) E(STATE)',
1 '-PARITY'/1X,'EXAMPLE 02P05 1.5+ (I2,A1,I2,1X,F3.1,A1)')
1500 FORMAT(1X,'NEXT TRY IS ',I2,A1,I2,1X,F3.1,A1)

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1400 FORMAT(1X,'TOO MANY OVERLAPS TO GET FIRST GUESS FOR',I3,A1,I2,F4
1.1,A1/1X,'VALUE OF ',F7.4,'*',F5.3,'=',F7.4,' WAS ASSIGNED',1X,
2'MANUALLY')
1500 FORMAT(1X,'FIRST GUESS FOR',I3,A1,I2,F4.1,A1,' IS',F6.2)
1600 FORMAT(///1X,'GUESSED MAXIMUM LINE DOES NOT APPEAR TO CORRELATE ',
1'WITH POINT OF'/1X,'MAXIMUM INTENSITY. MAXIMUM LINE GUESSED AS',
2I3,A1,I2,F4.1,' AT POINT',I6,' AND VALUE',F6.2/1X,'BUT MAXIMUM',
3' OCCURS AT POINT',I6,' WITH VALUE',F6.2,'. THE PRESENT ',
4'DECONVOLUTION'/1X,'INVOLVES THE FOLLOWING LINES:'/)
1700 FORMAT(1X,'NO.',I3,' TRANSITION',I3,A1,I2,F4.1,' AT POINT',I6)
1800 FORMAT(1X,'WHAT IS THE LINE NUMBER (FROM ABOVE) OF THE',1X,
1'TRANSITION THAT SHOULD'/1X,'BE USED AS THE MAXIMUM? (I1)')
1900 FORMAT(I1)
2000 FORMAT(1X,'THIS MAXIMUM LINE STILL DOES NOT ',
1'CORRELATE WITH'/1X,'THE LOCAL MAXIMUM. FOLLOWING ARE THE ',
2'INTENSITIES OF THE POINTS'/1X,'IMMEDIATELY BEFORE AND AFTER ',
3'THE POINT CORRESPONDING TO THE LINE'/1X,'CHOSEN AS MAXIMUM: '/
41X,10F7.2/1X,F7.2,I10,' INTENSITY AND POINT FOR MAX LINE'/
51X,10F7.2/1X,'INPUT THE POINT THAT SHOULD BE USED AS THE ',
6'MAXIMUM. (I5)')
2100 FORMAT(I5)
2200 FORMAT(1X,'TRANSITION',I3,A1,I2,F4.1,' AT POINT',I6,' WAS ',
1'MANUALLY DEFINED AS THE LINE'/1X,'WITH MAXIMUM INTENSITY FOR ',
2'THIS DECONVOLUTION. THIS RESULTED IN A SHIFT'/1X,'OF',I4,
3' POINTS TO ALIGN THE POINT OF MAXIMUM INTENSITY WITH THIS LINE.')
2300 FORMAT(//1X,'DECONVOLUTION FOR LINES',I4,' TO',I4,' (ALL LINES',1X
1,'SHIFTED',I3,' )'/1X,'INTENSITY VECTOR:',2X,10F7.3)
2350 FORMAT(1X,'FREQUENCY MATRIX:',2X,10F7.4,9(1/20X,10F7.4))
2400 FORMAT(1X,'SOLUTION:')
2500 FORMAT(1X,I3,A1,I2,F4.1,A1,' AT POINT',I6,' ASSIGNED INTENSITY OF'
1,F9.4)
IBCL=2
IBCR=2
FBCL=0.0
FBCR=0.0
KNTOP2=1
ITSK=1
IND=4
IDERV=0
KSL=0.964372825
IDX=INDX
NO=OVL(1,IDX)
LL=OVL(NO,IDX)
WRITE(6,1000) IDX,NO-1,LL
WRITE(7,1000) IDX,NO-1,LL
100 LOVL=LL
NTI=OVL(1,LL)
NTST=OVL(NTI,LL)
WRITE(6,1000) LL,NTI-1,NTST
WRITE(7,1000) LL,NTI-1,NTST
LL=NTST

```



```

IF (NTST.GT.LOVL) GO TO 100
YMAX=0.0
MAXJ=IDX
PAV=(FREQ(IDX)+FREQ(LOVL))/2.0
IPA=NINT(PAV/PSCL)
CALL LOCAL(IPA,YMNL,YAVL,YMXL,IPYMXL)
NC=0
PQMXL=REAL(IPYMXL)*PSCL
WRITE(7,1050) IDX,LOVL,YMNL,YMXL,IPYMXL,PQMXL
WRITE(6,1050) IDX,LOVL,YMNL,YMXL,IPYMXL,PQMXL
MS2=0
IPT(0)=0
SMPT(11)=11
DO 105 NDX=IDX,LOVL
INBV=1
WJ=FREQ(NDX)
IF (WJ.EQ.0.0) GO TO 105
NC=NC+1
NTRCK(NC)=NDX
IPT(NC)=NINT(WJ/PSCL)
IF (IPT(NC).EQ.IPT(NC-1)) GO TO 107
MSP=MSP+1
SMPT(MSP)=NC
107 IVJ=VUP(NDX)
BRJ=JE(NDX)
JLJ=JLOW(NDX)
CALL INTVAL(EST(NDX),BRJ,PRTY(NDX),N2,N3)
LMIN=ASSGN(1,IVJ,N3)
LMAX=ASSGN(2,IVJ,N3)
LC=1
LSTRT=LMAX
LEND=LMIN
LINC=-1
IF (BRJ.EQ.'R') THEN
LSTRT=LMIN
LEND=LMAX
LINC=1
END IF
IR=SORT(LSTRT,IVJ,N3,N2)
CALL SWITCH(LSTRT,IVJ,N3,N2,NP,IR,IS)
X(LC)=FREQ(IS)-20.0
IF (X(LC).LT.WMIN) X(LC)=WMIN
Y(LC)=YAVL
DO 115 K=LSTRT,LEND,LINC
IF (K.EQ.JLJ) THEN
KDX=LC
KINC=LC+1
GO TO 115
END IF
IR=SORT(K,IVJ,N3,N2)
CALL SWITCH(K,IVJ,N3,N2,NP,IR,IS)
IF (OVL(1,IS).EQ.0.OR.OVL(1,IS).GT.1) GO TO 115
LC=LC+1

```

```

      IF (OVL(1,IS).GT.0) GO TO 110
      WRITE(7,1100) IS,NDX
      WRITE(6,1100) IS,NDX
      IPK=NINT(FREQ(IS)/FSCL)
      Y(LC)=PTS(IPK)
      GO TO 112
110 CALL XVALUE(IS,IPK,YP)
      Y(LC)=YP
112 X(LC)=FREQ(IS)
115 CONTINUE
      IR=SORT(LEND,IVJ,NB,NE)
      CALL SWITCH(LEND,IVJ,NB,NE,NF,IR,IS)
      LC=LC+1
      X(LC)=FREQ(IS)+20.0
      IF (X(LC).GT.WMAX) X(LC)=WMAX
      Y(LC)=YAVL
      IF (LC.LT.4) GO TO 120
      WRITE(6,1150) NDX,KDX,KINC,(Y(K),K=1,LC)
      WRITE(7,1150) NDX,KDX,KINC,(Y(K),K=1,LC)
      CALL BINT4(X,Y,LC,IBCL,IBCR,PBCL,PBCR,KNTOPT,T,BCOEF,N,K,W)
      YGSS(NC)=EVALU(T,BCOEF,N,K,IDERV,WJ,INBV,WORX)
      GO TO 130
120 YG=YMXL-YMNL
      WRITE(6,1200) IVJ,BRJ,JLJ,EST(NDX),PTY(NDX),YG
      READ(5,1300) FRAC
      YGSS(NC)=FRAC*YG+YMNL
      WRITE(7,1400) IVJ,BRJ,JLJ,EST(NDX),PTY(NDX),YG,FRAC,YGSS(NC)
130 IF (YGSS(NC).GT.YMAX) THEN
      YMAX=YGSS(NC)
      MAXJ=NDX
      NCMX=NC
      END IF
      WRITE(7,1500) IVJ,BRJ,JLJ,EST(NDX),PTY(NDX),YGSS(NC)
      WRITE(6,1500) IVJ,BRJ,JLJ,EST(NDX),PTY(NDX),YGSS(NC)
105 CONTINUE
      SMPT(MSP+1)=SMPT(MSP)+(LOVL-NTRCK(SMPT(MSP))+1)
      ISHFT=IPT(NCHX)-IPYMXL
      IF (IABS(ISHFT).GT.2.0E.YMXL.GT.1.5*YMAX) THEN
      WRITE(6,1600) VUP(MAXJ),BR(MAXJ),JLOW(MAXJ),EST(MAXJ),IPT(NCHX),
1YMAX,IPYMXL,YMXL
      DO 140 MJ=1,NC
      MNJ=NTRCK(MJ)
      WRITE(6,1700) MJ,VUP(MNJ),BR(MNJ),JLOW(MNJ),EST(MNJ),IPT(MJ)
140 CONTINUE
      WRITE(6,1800)
      READ(5,1900) MJ
      MNJ=NTRCK(MJ)
      ISHFT=IPT(MJ)-IPYMXL
      IF (IABS(ISHFT).GT.2) THEN
      IPC=IPT(MJ)

```

```

DO 145 JN=1,21
JNJ=IPC+JM-11
PCJ(JN)=PTS(JNJ)
145 CONTINUE
WRITE(6,2000) (PCJ(J),J=1,10),PCJ(11),IPC,(PCJ(JJ),JJ=12,21)
WRITE(7,2000) (PCJ(J),J=1,10),PCJ(11),IPC,(PCJ(JJ),JJ=12,21)
READ(5,2100) IPYMXL
ISHFT=IPT(MJ)-IPYMXL
END IF
WRITE(7,2200) VUP(MNJ),BR(MNJ),JLOW(MNJ),EST(MNJ),IPT(MJ),ISHFT
END IF
DO 170 JN=1,MSP
JNJ=SMPT(JN)
J=NTRCK(JNJ)
IREL=IPT(JNJ)-ISHFT
B(JN)=PTS(IREL)-YAVL
DO 175 JJN=1,MSP
NJJ=SMPT(JJN)
JJ=NTRCK(NJJ)
DLTFRQ=REAL(IPT(JNJ)-IPT(NJJ))/4.0
P(JJN,JN)=EXP(-DLTFRQ**2)
175 CONTINUE
170 CONTINUE
WRITE(6,2300) IDX,LOVL,ISHFT,(B(J),J=1,MSP)
WRITE(6,2350) ((P(K,L),L=1,MSP),K=1,MSP)
WRITE(7,2300) IDX,LOVL,ISHFT,(B(J),J=1,MSP)
WRITE(7,2350) ((P(K,L),L=1,MSP),K=1,MSP)
CALL SPOFS(P,MSP,MSP,B,ITSK,IND,K)
WRITE(6,2400)
WRITE(7,2400)
DO 190 JJ=1,MSP
JNJ=SMPT(JJ)
J=NTRCK(JNJ)
IPTS=IPT(JNJ)
PTS(IPTS)=B(JJ)+YAVL
IF (PTS(IPTS).LT.0.0) PTS(IPTS)=YAVL
YASGN(J)=PTS(IPTS)
190 CONTINUE
DO 185 IJ=1,MSP
MPS=SMPT(IJ+1)-SMPT(IJ)
IF (MPS.EQ.1) GO TO 185
JMP=SMPT(IJ)
JM=NTRCK(JMP)
IPTS=IPT(JMP)
TOT=PTS(IPTS)
YGTOT=0.0
DO 190 JI=1,MPS
JP=JMP+JI-1
YGTOT=YGTOT+YGBS(JP)
190 CONTINUE

```

```

DO 135 JI=1,MPS
JP=JAP+JI-1
JA=NTRCK(JP)
YASGN(JM)=TOT*YGSS(JP)/YGTOT
195 CONTINUE
135 CONTINUE
DO 200 IJ=1,NC
J=NTRCK(IJ)
IPTS=IPT(IJ)
OVL(1,J)=-OVL(1,J)
WRITE(6,2500) VJP(J),BR(J),JLOW(J),ZST(J),PRTY(J),IPTS,YASGN(J)
WRITE(7,2500) VJP(J),BR(J),JLOW(J),ZST(J),PRTY(J),IPTS,YASGN(J)
200 CONTINUE
RETURN
END
C *****SWITCH*****
SUBROUTINE SWITCH(MJ,MV,MB,ME,MF,MR,MS)
INTEGER*4 SORT
DIMENSION FREQ(1450),SORT(0:50,10,3,4)
COMMON/OSWXV/ FSCL,FREQ,SORT
MS=MR
IF (ME.EQ.1.OR.ME.EQ.3) THEN
MF=ME+1
ELSE
MF=ME-1
END IF
IF (FREQ(ME).NE.0.0) GO TO 100
MS=SORT(MJ,MV,MB,MF)
100 CONTINUE
RETURN
END
C *****XVALUE*****
SUBROUTINE XVALUE(INDX,IPNT,YP)
INTEGER*4 SORT
DIMENSION PTS(16400),RDV(16400)
DIMENSION FREQ(1450),SORT(0:50,10,3,4)
COMMON/OSWXV/ FSCL,FREQ,SORT
COMMON/N16K/ AVRG,YARDV,PTS,RDV
IP=NINT(FREQ(INDX)/FSCL)
YP=0.0
IST=IP-3
IPNT=IP
DO 100 I=1,7
IF (PTS(IST).GT.YP) THEN
YP=PTS(IST)
IPNT=IST
END IF
IST=IST+1
100 CONTINUE
RETURN
END

```

```

C ***** LOCAL
  SUBROUTINE LOCAL(MPT,YMNL,YAVL,YMXL,IPYMXL)
    DIMENSION PTS(16400),RDV(16400)
    COMMON/N16K/ AVRG,YMRDV,PTS,RDV
    YMNL=1.5*AVRG/RDV(MPT)
    YMNA=YMRDV/RDV(MPT)
    YMXL=PTS(MPT)
    IPYMXL=MPT
    YAVL=0.0
    CNT=0.0
    DO 100 IBS=1,40
      IF (PTS(MPT+IBS).LT.YMNL) YMNL=PTS(MPT+IBS)
      IF (PTS(MPT-IBS).LT.YMNL) YMNL=PTS(MPT-IBS)
      IF (IBS.GT.4) GO TO 100
      IF (PTS(MPT+IBS).GT.YMXL) THEN
        YMXL=PTS(MPT+IBS)
        IPYMXL=MPT+IBS
      END IF
      IF (PTS(MPT-IBS).GT.YMXL) THEN
        YMXL=PTS(MPT-IBS)
        IPYMXL=MPT-IBS
      END IF
100  CONTINUE
      YACP=6.0*ABS(YMNL-YMNA)
      DO 400 IBS=1,40
200  YTST=ABS(PTS(MPT+IBS)-YMNA)
      IF (YTST.GT.YACP) GO TO 300
      CNT=CNT+1.0
      YAVL=YAVL+PTS(MPT+IBS)
300  YTST=ABS(PTS(MPT-IBS)-YMNA)
      IF (YTST.GT.YACP) GO TO 400
      CNT=CNT+1.0
      YAVL=YAVL+PTS(MPT-IBS)
400  CONTINUE
      IF (CNT.GT.0.0) THEN
        YAVL=YAVL/CNT
      ELSE
        YAVL=AVRG/RDV(MPT)
      END IF
      RETURN
    END
C*****FLTI2*****
    REAL*4 FUNCTION FLTI2 (I2)
    INTEGER*2 I2
    INTEGER*4 I4
    I4 = I2
    FLTI2 = FLOAT (I4)
    RETURN
  END

```

Appendix A.3

Figures A1 and A2 illustrate the earliest observed rotational distributions of the HCl product from reaction of O^* with CH_3Cl (figure A1) as well as the HCl rotational relaxation in the $v' = 1$ level for the same reaction (figure A2). The measured rotational populations were obtained from the P-branch of the HCl emission, for which the J' -level is defined as the lower state. Therefore the first rotational state label is 1, even though the upper emitting rotational state has $J' = 0$.

Initial Rotational Populations of HCl from CH_3Cl

Figure A1: Relative rotational populations for vibrational levels 1 to 5 for the HCl from the reaction $\text{O}^* + \text{CH}_3\text{Cl}$ at the earliest observation time.

Rotational Populations of HCl($v'=1$) from CH₃Cl

Figure A2: Time evolution of the relative rotational populations for $v' = 1$ from the reaction $O^* + CH_3Cl$. The average number of gas kinetic collisions is given in the legend for each set of curves.

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