



Direct vs complex reaction dynamics for F+OH \rightarrow HF+O

J. J. Sloan, D. G. Watson, J. M. Williamson, and James S. Wright

Citation: The Journal of Chemical Physics **75**, 1190 (1981); doi: 10.1063/1.442167 View online: http://dx.doi.org/10.1063/1.442167 View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/75/3?ver=pdfcov Published by the AIP Publishing

Articles you may be interested in

Mode specificity in the HF + OH \rightarrow F + H2O reaction J. Chem. Phys. **141**, 164316 (2014); 10.1063/1.4900445

Quasiclassical Trajectory Study of F+H2O→HF+OH Reaction: Influence of Barrier Height, Reactant Rotational Excitation, and Isotopic Substitution Chin. J. Chem. Phys. **26**, 627 (2013); 10.1063/1674-0068/26/06/627-634

Spin-orbit corrected full-dimensional potential energy surfaces for the two lowest-lying electronic states of FH2O and dynamics for the F + H2O \rightarrow HF + OH reaction J. Chem. Phys. **138**, 074309 (2013); 10.1063/1.4791640

Low energy ion–molecule reaction dynamics: Complex and direct collisions of O- with NH3 J. Chem. Phys. **97**, 4008 (1992); 10.1063/1.462940

Effect of enhanced collision energy on product vibrational excitation for the proton transfer reaction: $O-+HF\rightarrow F-+OH(v=0,1)$ J. Chem. Phys. **96**, 298 (1992); 10.1063/1.462518



Direct vs complex reaction dynamics for $F+OH\rightarrow HF+O$

J. J. Sloan

Division of Chemistry, National Research Council of Canada, Ottawa, Canada K1A 0R6

D. G. Watson, J. M. Williamson,^{a)} and James S. Wright

Department of Chemistry, Carleton University, Ottawa, Canada K1S 5B6 (Received 1 December 1980; accepted 15 April 1981)

The exerogicity of the reaction $F + H_2O \rightarrow HF + OH$ is sufficient to give $HF(v' \le 1)$; however, arrested relaxation infrared chemiluminescence experiments on this system show emission from $HF(v' \le 3)$. The higher vibrational levels are populated by the secondary reaction $F(^2P) + OH(^2II) \rightarrow HF(^1\Sigma^+) + O(^3P)$. By a combination of SCF-CI calculations and a rotated Morse curve fitting procedure, it is shown that barrier heights on triplet surfaces which correlate reactants and products of the secondary reaction are too high to provide a reaction path. Instead, the reaction proceeds on a singlet surface to produce an HOF complex, followed by rearrangement and a nonadiabatic transition to the triplet surface. An exit-channel barrier results from the surface crossing. The chemiluminescence data are shown to be in accord with this reaction mechanism.

I. INTRODUCTION

In the gas-phase collisions of fluorine atoms with small molecules, almost all reactions studied to date show nascent product vibrational energy distributions which are highly nonstatistical, and often inverted. A summary of these data has been given by Bogan and Setser¹ for reactions of F + R - H - HF + R. These nonstatistical distributions are generally assumed to result from direct abstraction reactions having very small activation barriers and very short interaction times.

Recently some reactions have been reported which show statistical or near-statistical product vibrational energy distributions. One such example is the branching reaction F + DCOOH which gives products HF(v', J')+ DCOO and DF(v', J') + COOH. It was found that the HF(v') populations are statistical but DF(v') populations are inverted.² These results were interpreted as being due to formation of a long-lived complex at the carboxyl group, with subsequent energy randomization prior to formation of HF, whereas reaction at the C-D bond is a direct abstraction of short duration. Another example from this laboratory³ is production of HF from $F + HN_3$, where again the nearly statistical vibrational distribution was thought to be the result of complex formation.

Experimental and theoretical studies of the reaction

 $O(^{1}D) + H_{2} - OH(^{2}\Pi) + H$

have contributed significantly to the understanding of complex versus direct reaction dynamics. The OH vibration-rotation populations for v' = 0 and 1 were measured by Smith and Butler⁴ and Luntz *et al.*⁵ They found a nearly statistical ratio of v' = 1 to v' = 0, but a highly nonstatistical rotational distribution. This reaction exhibits microscopic branching, since collinear O-H-H abstraction competes with insertion of O into the H-H bond. Trajectory calculations of Whitlock *et al.*, ⁶ Sorbie and Murrell, ⁷ and Schinke and Lester⁸ on empirical^{6,7} and fitted *ab initio* potential surfaces⁸ indicated that abstraction produces hot v', cold J' distributions whereas insertion produces cold v', hot J' distributions. Due to the presence of a small barrier along the abstraction path, the insertion route is dominant, leading to product OH energy distributions in agreement with the experimental results.^{4,5}

In this paper we report in Sec. II the results of an arrested relaxation IR-chemiluminescence study of the reaction of F + OH. The OH radical is generated in the primary reaction

 $F + H_2O - HF(v', J') + OH, \quad \Delta H_0^0 \approx -17.4 \text{ kcal mol}^{-1}, (1)$

followed by the secondary reaction

F + OH
$$\rightarrow$$
 HF (v', J') + O $({}^{3}P), \Delta H_{0}^{0} = -33.7 \text{ kcal mol}^{-1}$ (2)

The product energy distribution from Reaction (2) is consistent with a nearly statistical vibrational distribution, suggesting complex formation, with subsequent rearrangement to products; this route appears to be preferred over the abstraction $F \cdots H \cdots O$. By use of state correlation diagrams and extensive SCF-CI calculations we show in Secs. III-V that the reaction of F + OH probably involves a *spin-forbidden transition* from a singlet to a triplet potential surface. It is shown in Sec. VI that this mechanism is consistent with the observed emission data.

II. EXPERIMENT

The apparatus consists of an arrested relaxation infrared chemiluminescence machine which has been described previously.² For the purposes of the present experiment, the reagent inlet configuration shown in Ref. 2 is replaced by a "prereactor" inlet device⁹ which produces the OH chemically. To generate the OH we chose the reaction $F + H_2O - OH + HF$ because this method ensures that no H_2 is present in the system, thus preventing the $F + H_2$ reaction from constituting an interference in the subsequent measurements.

The prereactor consists of a 2.5 cm i.d. Teflon tube having a 4 mm diameter quartz tube on its central axis.

130.18.123.11 On: Tue, 23 Dec 2014 17:42:25

^{a)}Present address: Department of Chemistry, University of Toronto, Canada.

	CF ₄ flow	H ₂ O flow			Population	
Experiment	(μ m	ol s ⁻¹)	Ar flow	<i>v</i> ′ = 1	v '=2	<i>v</i> '=3
36	6.5	19.4	2	0.931	0.060	0.009
38	13.5	13.3	2	0.873	0.109	0.017
39	13.5	13.7	0	0.890	0.097	0.013
40	6.4	1.1	0	0.793	0.17 3	0.0 34

TABLE I. Experimental conditions and HF vibrational populations.

The end of the latter tube is sealed, and five 1 mm diameter holes are drilled through its wall near the sealed end. The axial position of the central tube can be adjusted such that these holes can be located at any point from about 1 cm outside the end of the Teflon tube to about 1.5 cm inside it. The H₂O is admitted via the central tube. It is injected laterally into a stream of F atoms flowing down the Teflon tube. The F atoms are generated in a 100 W, 2450 MHz discharge in CF_4 (Matheson 99.7%).

At the mixing point, near the H_2O injection holes the pressure is about 1–10 mTorr, depending on the axial position of the central tube and on the reagent flow rates. The reaction products and unused reagents expand into an observation region defined by a multipass light gathering cell. The bottom of the Teflon tube is located about 1.5 cm above the level of the tops of the two (first surface, gold-coated) mirrors comprising this cell. The infrared emission collected by the cell is recorded by a Fourier transform infrared spectrometer. Normally, the average pressure at the central axis of the multipass cell is in the 10⁻⁵ Torr range. In these experiments, the flow of F atoms is made sufficiently large that some F atoms remain after Reaction (1) to react with the OH product.

The behavior of the HF product energy distribution is recorded as a function of reagent flows and location of the H₂O injection point. The experimental parameters and HF vibrational distributions for four experiments are listed in Table I. For all these experiments, the H₂O injector was at its lowest position (approximately level with the bottom of the Teflon tube). No effect is observed on raising the injector by up to 5 mm. Raising it further causes the v' = 1/v' = 2 population ratio to increase systematically. The v' = 2/v' = 3 population ratio changes more slowly on raising the injector than does the ratio of P(v'=1) to either of the other two populations.

The experiment must detect and identify the products of reaction among other possible processes, and it must ensure that the OH reagent from Reaction (1) is without appreciable internal excitation. The latter requirement arises because it is necessary to distinguish between reaction on the F-H-O triplet surface which contains an appreciable barrier, and reaction on the F-O-H singlet surface which has no barrier but requires a transition to the triplet surface in the exit channel (see Sec. VI). In order to ensure that the OH from Reaction (1) is translationally thermalized before the subsequent reaction, experiments were performed with a wide range of reagent flows and (in some cases) with the addition of some argon for the H_2O flow. In these experiments, it was judged that the OH reagent in Reaction (2) had been translationally thermalized if there was no variation in either the highest population vibrational state of HF (v' = 3) or in the v' = 2/v' = 3 HF population ratio. Both of these observables depend only on Reaction (2), and if they varied with the different reagent flows, it would indicate either incomplete OH thermalization or extensive collisional energy transfer in the HF product of Reaction (2). Neither of these conditions is acceptable in this experiment.

III. EXPERIMENTAL RESULTS

The HF emission spectrum measured in experiment 40 (see Table II) is shown in Fig. 1. The complete spectrum is shown in Fig. 1(a). The lower half, Fig. 1(b), shows an enlargement of the region containing the $v' \ge 2$ emission. The vibrotational population distributions, P(v'J'), obtained from this spectrum are shown in Fig. 2. The continuous curves connecting the tops







FIG. 2. Vibration-rotation populations for HF from experiment 40. v''=1 (lower panel) dotted curve -300 K Boltzmann distribution. v'=2, 3 dotted curves—statistical rotational distributions.

of the vertical lines (representing the rotational populations) are natural cubic splines, inserted to aid visualization. The vibrational distributions $P(v') \propto \sum_{J'} P(v', J')$ are shown in Fig. 3. The occurrence of Reaction (2) may be deduced from the fact that emission is detected from all vibrational states HF ($v' \leq 3$), whereas Reaction (1) can (thermochemically) populate only HF (v' < 1).

A further indication that Reaction (2) is the origin of the v'=2 and v'=3 emission is given by the fact that the highest energy level observed in emission is v' = 3. J'=6, which has an energy (E'_{tot}) of 34.08 kcal mol⁻¹. Due to possible overlapping of the spectral lines involved, and to the relatively low signal to noise here. we put an uncertainty of ± 1 J' level on this identification. Assuming that the activation energy E_a for Reaction (2) is approximately zero, as would be expected for a radical-radical reaction, then the equation¹⁰ $E'_{tot} = E_a$ $+5/2RT - \Delta H_0^0$ (where 5/2RT gives the average reagents thermal energy) permits calculation of the reaction excergicity, ΔH_0^0 , and hence the bond strength of the reagent (using D_0 (HF) = 135 kcal mol⁻¹).¹¹ This procedure gives a value between 101.0 and 102.4 kcal mol⁻¹, which coincides with the currently accepted value of the OH bond strength $(D_0 = 101.3 \pm 0.5 \text{ kcal mol}^{-1})$.¹¹

The suggestion that the HF (v'=2) and (v'=3) emission originates from a secondary reaction rather than HF/HF vibrational up-pumping is also supported by the fact that all experiments in Table I show the same value of this cutoff (v'=3, J'=6) within $\pm 1 J'$ -state. If the higher vibrational levels were created by energy transfer processes, the cutoff would be expected to vary with the HF vibrational population distribution, and hence, with reagent flows.

The experimental data also indicate that the OH reagent in Reaction (2) must be very nearly room temperature in all its degrees of freedom. First, as regards vibrational excitation—we see no OH (v'=1+0) emission in any spectra, although the HF (v'=1+0) signal was seen with a signal-to-noise ratio greater than 180. Although the Einstein transition probability for OH is about a factor of 12 smaller than HF, ¹² our detector (InSB, 77 K) is about 1.5 times more sensitive in the OH (1-0) region than for the corresponding HF transition. This indicates that the concentration ratio of OH (v=1)/HF (v=1) in our system must be less than 0.05, and therefore that virtually all of the OH is in the v=0 state.

We also believe that the OH rotational temperature must be approximately 300 K. The rotational distribution of the HF (v' = 1) emission shown in the lower panel of Fig. 2 is accurately fitted by a 300 K Boltzmann distribution, shown as a dotted curve in the figure. Since the OH and the majority of the HF (v' = 1) products are formed in the same region by Reaction (1), both would have the same number of collisions on flowing out of this reaction zone. Since the rotational energy transfer characteristics of most diatomic hydrides are similar, ¹³ it is unlikely that the HF could be rotationally thermalized without the OH being so also.

These data also indicate that the OH must be translationally thermalized to 300 K before undergoing Reac-



FIG. 3. Vibrational population distributions for HF from experiment 40.

tion (2), since translational relaxation is much more rapid than rotational thermalization. This is further suggested by the constancy of the observed cutoff (v'= 3, J' = 6) mentioned previously. If the OH reagent in Reaction (2) were translationally excited, the extra energy would appear as an increase in the maximum internal excitation¹⁴ and the highest populated state would be a function of the extent of the OH relaxation (i.e., the reagent flows).

Finally, we note that the HF (v'=2) and (v'=3) distributions shown in Figs. 2 and 3 are not necessarily the "initial" or completely unrelaxed results from Reaction (2). The very small population of (v'=3) (and hence its poor signal to noise ratio) makes it difficult to establish P(v'=2)/P(v'=3) ratios which are completely insensitive to reagent flows. The calculations presented in subsequent sections deal with Reaction (2) but do not depend on the precise details of its initial product energy distribution.

IV. METHOD OF CALCULATION

Our CI calculations use the MRD-CI method and program described in previous publications.^{15,16} The method makes use of multiple reference configurations in the configuration interaction calculation, and uses an extrapolation technique to obtain an estimate of the CI energy based on the inclusion of all single and double excitations from the reference configurations. This result is termed the MRD-CI energy. The final energy, denoted F-CI, is obtained by making the multireference analog of the Davidson correction¹⁷ to the MRD-CI eigenvalue, thereby allowing an estimate of the effect of quadruple excitations from all reference configurations. Two basis sets are used in this study. The first is the split-valence 4-31 G basis set of GTO's used in the Gaussion 70 program¹⁸ of Pople and co-workers.¹⁹ This basis set is suitable for rough scans of the various surfaces to locate the important features and to determine which configurations dominate the CI wave function. A larger double-zeta + polarization (DZP) basis set of GTO's uses the Dunning (9s 5p 1d/4s 2p 1d) contraction of GTO's on oxygen and fluorine, with s, p exponents from Huzinaga²⁰ and d exponents from Hay and Dunning.²¹ The hydrogen (4s1p/2s1p) exponents and contraction are also given by Hay and Dunning. The DZP basis set is used where high accuracy is desired.

In all the split-valence calculations, the CI was based on excitation to and from all available orbitals. In the DZP calculations the oxygen and fluorine core orbitals (and their high-energy complements) were kept frozen in the CI. The number of reference configurations in the CI varied from one to four, depending on which region of surface was being studied. The highest number of configurations was needed to describe the region of the transition state, where a configuration change generally occurs. Also, more configurations were needed to describe highly dissociated geometries. In practice reference configurations were added whenever their (squared) contribution to the final CI wave function exceeded 1%. In this way, the contribution of all reference configurations to the final CI wave function remained approximately constant at 95%, which helps to ensure a balanced treatment over the entire surface. A CI selection threshold^{15,16} of 50 μ hartree was employed for all calculations, except as otherwise noted.

In this study we are interested in the potential surfaces for linear $F \cdots H \cdots O$, both singlet and triplet, and in the bent ground state FOH. For the linear surfaces the rotated Morse curve-spline method (RMCS)²² is used to select the location of the *ab initio* points. The fitting procedure is identical to that which was used to obtain an *ab initio* surface for H₂O, ²³ except that the lower symmetry in the FHO system requires more data points. Briefly, the RMCS method begins with the definition of a "swing point", which is in the triatomic dissociation region (chosen here as $R_{FH} = R_{OH} = 10$ bohr). The RMCS polar coordinate θ and distance coordinate l are defined in terms of the swing point and the internal coordinates R_{FH} and R_{OH} (see Fig. 5). The assumption is made that a Morse curve along each ray θ describes the variation of the potential energy, provided that the Morse parameters $D(\theta)$, $\beta(\theta)$, and $l_{e}(\theta)$ are reoptimized along each ray. At each θ -value from three to six F-CI energies are computed and compared to the energy zero (swing point). This establishes V at each l. A nonlinear least square fit to the RMCS function

$$V = D\{1 - \exp[\beta(l - l_{e})]\}^{2} - D$$

establishes the Morse parameters $D(\theta)$, $\beta(\theta)$, and $l_{\theta}(\theta)$.

One-dimensional natural cubic splines interconnect the parameter values at each θ so that D, β , and l_e become continuous functions of θ . In the noninteraction regions $0 \le \theta \le 25^\circ$ and $65 \le \theta \le 90^\circ$, additional values of D, β , and l_e are artificially generated according to exact relations.^{22,23} The spline fits are examined and the data are smoothed, if necessary, to remove any unphysical oscillations. In this way a continuous potential surface is generated. The quality of the fit can be established by considering the overall standard deviation and the error limits in the Morse parameters along each ray. If the Morse fits are good, then the minimum energy path is accurately described and such features as wells or barriers along the reaction path will necessarily also be accurately described, provided that the θ grid is sufficiently fine. The RMCS-CI approach was found in a previous study²³ to give an excellent fit to ab*initio* data for the singlet surface $H_2O \rightarrow OH(^2\Pi) + H(^2S)$.

V. POTENTIAL SURFACES

A correlation diagram which connects reactant states $F(^{2}P) + OH(^{2}\Pi)$ to product states $HF(^{1}\Sigma^{*}) + O(^{3}P)$ and $HF(^{1}\Sigma^{*}) + O(^{1}D)$ is shown in Fig. 4. The relative energy levels are drawn as shown because $HF + O(^{3}P)$ is exothermic relative to reactants by 34 kcal mol⁻¹, $O(^{1}D)$ lies 45 kcal mol⁻¹ above $O(^{3}P)$, ²⁴ and HOF is a bound, stable molecule. The upper four lines assume a linear approach $F \cdots H \cdots O$ requiring C_{wv} symmetry, whereas the lowest energy C_{s} approach leads to the nonlinear HOF molecule. For singlet and triplet states, the correlations between symmetry types for C_{wv} and C_{s} groups are: $\Sigma^{*} + A'$, $\Sigma^{-} + A''$, $\Pi + A' + A''$, $\Delta + A' + A''$. Using



FIG. 4. Schematic correlation diagram for $F + OH \rightarrow HF + O$.

labels appropriate to nonlinear approaches results in a correlation diagram identical to that given by Addison *et al.*²⁵

As shown in Fig. 3, the ${}^{3}\Pi$ and ${}^{3}\Sigma^{-}$ surfaces connect ground state reactants to ground state products, whereas the singlet surfaces ${}^{1}A'$, ${}^{1}\Pi$, and ${}^{1}\Delta$ correlate to excited state products. Some justification for the optimum approaches for the various states (linear vs. nonlinear) can be gained from the potential surfaces obtained by Howard, McLean, and Lester²⁶ (hereafter HML) for the analogous (reversed) reactions $O({}^{1}D, {}^{3}P) + H_{2} \rightarrow OH({}^{2}\Pi)$ + H (^{2}S). For the $^{3}\Pi$ and $^{1}\Pi$ states, corresponding to abstraction $O \cdots H \cdots H$, the lowest barriers occurred in the linear path. No barrier was encountered for $O(^{1}D)$ approaching H-H along the $C_{2\nu}$ insertion path, resulting in the deep $H_2O({}^1A')$ potential well. Based on these results, we assume in our work that the abstraction paths $F \cdots H \cdots O$ are linear (leading to ${}^{3}\Pi, {}^{3}\Sigma^{*}$. ${}^{1}\Pi$, and ${}^{1}\Delta$ states) and that a nonlinear path results in formation of the deep HOF well $({}^{1}A')$.

Because the reactants $F({}^{2}P)$ and OH (${}^{2}\Pi$) are thermalized prior to reaction, and the product state HF + O (${}^{1}D$) is endoergic by 11 kcal mol⁻¹, formation of HF + O (${}^{1}D$) is energetically inaccessible. The ${}^{1}\Pi$ and ${}^{1}\Delta$ states will therefore play no role if it can be shown that these states do not cross lower-lying triplet states in a way which could allow the triplet barriers to be avoided. Establishing the height and location of the triplet barriers is clearly very important, and we now discuss the various surfaces.

A. Singlet FHO surfaces

1. ¹ Δ surface. Considering just the valence electrons, the ¹ Δ surface contains eight electrons in the σ system, and the π system has configuration $(\pi_u)^4 (\pi_d^*)^2$. In this state two electrons occupy an antibonding orbital, but this destabilization is weakened since H lies between F and O.

Since we require only the general shape of the ${}^{1}\Delta$ surface, the small 4-31 G basis set was used. Also, because this surface is less critical to the arguments which follow, we report fewer details of the calculation. The calculated atomic and molecular energies are shown in Table II. From this table we derive the energy of the swing point $F(^{2}P) + H(^{2}S) + O(^{1}D)$, corresponding to the dissociation limit on the singlet surfaces, of -174.4730hartree (using F-CI values). The diatomic bond distances used in Table II are experimental values from Herzberg.²⁴ The F-CI calculation for FHO with R_{OH} = 1.833 bohr and $R_{HF} = 10.0$ bohr yields -174.6808hartree, in good agreement with the F-CI result of -174.6799 hartree for the fragments $F(^{2}P) + OH(^{2}\Pi)$. This provides a useful consistency check on the CI calculation, since the triatomic calculation should smoothly approach the atom-diatom limit on dissociation.

From Table II, the reaction $F(^{2}P) + OH(^{2}\Pi) \rightarrow HF(^{1}\Sigma^{*}) + O(^{1}D)$ is endoergic by 25.5 kcal mol⁻¹, whereas $F(^{2}P) + OH(^{2}\Pi) \rightarrow HF(^{1}\Sigma^{*}) + O(^{3}P)$ is excergic by 26.7 kcal $\times mol^{-1}$, so that the calculated ³P and ¹D oxygen states are separated by 52.2 kcal mol⁻¹. The corresponding experimental values (corrected for zero-point energy differences between HF and OH) are + 10.3 kcal mol⁻¹ and - 35.1 kcal mol⁻¹, giving a separation of 45.2 kcal $\times mol^{-1}$. Thus, it can be seen that while the 4-31 G basis set gives qualitatively correct results, the quantitative agreement with experimental values is poor. Nevertheless, due to the correct dissociation properties of the CI calculation, the general shape of the surface should be correct.

The RMCS parameters were chosen as follows: swing point at $(10a_0, 10a_0)$, bond angle 180°, θ values of 0, 30, 35, 40, 43, 45, 47, 50, 55, 60, and 90°. Four to six F-CI data points were used along each θ -ray. Values of the distance *l* along each ray were chosen so as to

TABLE II. Calculated atomic and molecular energies using the 4-31G basis set, for the linear system $F \cdots H \cdots O$. Distances are in bohr, energies in hartree.

Species	Geometry	SCF energy	Main	MRD-CI energy	F-CI energy
$F(^2P)$	•••	- 99. 2649	1	- 99.3511	- 99.3527
H(² S)	•••	-0.4968	1	-0.4968	-0.4968
O(³ P)	•••	- 74.6451	1	- 74. 7055	- 74. 7066
$O(^{1}D)$	•••	- 74. 5223	3	- 74.6213	- 74.6235
ОН(² П)	1.832	- 75.2278	1	- 75.3258	- 75.3272
HF(¹ Σ*)	1.720	- 99. 8879	1	- 100, 0153	- 100.0158
FHO(¹ Δ)	1.833, 10.0	- 174. 4927	2	- 174. 6730	- 174. 6808

This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP:



FIG. 5. RMCS plots for ${}^{1}\Delta$ surface, for (a) Well depth D, (b) shape parameter β , (c) distance to minimum energy path l_{e} .

obtain a range in the Morse potential of 1.0-1.5 eV. The rms deviation of the Morse fits from the F-CI values were then computed along each ray. These results are summarized in Table III, where it is seen that the Morse fits along each ray are of a quality comparable to that achieved at $\theta = 0$ (corresponding to HF + O) and $\theta = 90$ (F + OH), where good Morse curves are expected. This justifies the assumption that rotated Morse curves can represent the entire surface.

Plots of $D(\theta)$, $\beta(\theta)$, and $l_e(\theta)$ are shown in Figs. 5(a)-5(c). Data points indicated by an x are in the non-interaction region and were generated as described in Ref. 22. The actual data points contain some scatter arising from the uncertainty in the MRD-CI extrapolation to the full single and double-excitation limit, and in the least-squares data fit to F-CI values.

Natural cubic splines were fitted to the data points (solid line, Fig. 5). Some nonphysical oscillations of the spline are evident in Fig. 5(a) near $\theta = 35^{\circ}$, but these effects are small and were removed by slight smoothing. Small potential wells (~1 kcal mol⁻¹) are encountered near 35 and 55°, and a large barrier of 46 kcal mol⁻¹ near $\theta = 43^{\circ}$.

The location of the energy barrier is seen in Fig. 6, which shows a contour map of the RMCS-CI potential surface. This map reveals the essential features of the (endothermic) reaction. The high barrier and increasing energy enroute to the transition state shows that the $^{1}\Delta$ surface should not participate in the reaction which produces O (³P).

2. ¹II surface. This state is formed from the piconfiguration $(\pi_u)^4 (\pi_e^*)^3$. Since the highest occupied sigma-MO is essentially nonbonding, this state is probably of higher energy than ¹ Δ in the strong interaction



FIG. 6. RMCS potential surface for ${}^{1}\Delta$ state with geometry $F \cdots H \cdots O$. The outer contour is at -2.0 eV relative to $F + H + O({}^{1}D)$, contour spacing is 0.5 eV. The (θ, l) coordinate system and minimum energy path are also shown.

θ (deg)	D(eV)	$\beta (a_0^{-1})$	$l_{e}\left(a_{0}\right)$	No. of peaks ^a	rms deviation (eV)	Range of data (eV)
0	4,612	1.249	8.216	5	0.002	0.8
30	4.678	1.116	9,489	5	0.006	0.9
35	4,631	0.986	10,022	4	0.003	0.8
40	4, 521	0,967	10.644	5	0.010	0.8
43	3.728	0,875	10.900	6	0.010	0.5
45	3.864	0.723	10.761	5	0.004	0.9
47	4.856	0.771	10.809	4	0.002	1.5
50	5.583	0.809	10.555	5	0.012	1.0
55	5,747	0.873	9.928	5	0,010	0.8
60	5,689	0.934	9,399	5	0.006	1.2
90	5.731	1.113	8.134	5	0.009	2.5

TABLE III. Rotated Morse curve data, to be used as input to cubic spline functions.

^aIn addition to the swing point, which has a weighting factor of 2.

region. Also, HML found the ${}^{1}\Pi$ state in $H \cdots H \cdots O$ to be more repulsive than the ${}^{3}\Pi$, which had a barrier height of 14 kcal mol⁻¹. For these reasons, this state will not be considered further.

3. ¹A' surface. The ¹A' state is strongly bound in the bent F^{-O-H} geometry. The HOF molecule is known experimentally²⁷ to have a bond angle of 96.8°, with R_{OH} = 0.966 Å and R_{OF} = 1.442 Å. The optimum equilibrium structure has been the subject of previous SCF²⁸ and MRD-CI²⁹ calculations. For our purposes, we compute the energy of a single point at the experimental geometry, using the 4-31 G basis. The result of this calculation is an SCF energy of -174.4563 hartree and an F-CI energy of -174.7231 hartree. The binding energy relative to $F(^{2}P) + O(^{1}D) + H(^{2}S)$ is therefore 157 kcal \times mol⁻¹, and 105 kcal mol⁻¹ relative to products with $O({}^{3}P)$. The binding is always underestimated by 20-30% at this level of treatment, but this definitely shows the deep potential well. This then represents the most stable form of the "complex" which can be formed from F + OH.

B. Triplet FHO surfaces

1196

1. ${}^{3}\Pi$, 4-31 *G* basis. For the linear geometry $F \cdots H \cdots O$, abstraction of H by F can occur on the ${}^{3}\Pi$ surface. In addition to the $H \cdots H \cdots O {}^{3}\Pi$ surface results of HML quoted earlier, where a barrier of 14 kcal mol⁻¹ was found, this linear path was also found by

Walch *et al.*, 30 to be the least-energy approach. Since the ³II barrier height is essential to our conclusions, we report the RMCS-CI results in greater detail.

The reactants $F(^{2}P) + OH(^{2}\Pi)$ now correlate to $HF(^{1}\Sigma^{*})$ $+O(^{3}P)$, and the swing point (dissociation limit) is the F-CI energy of $F(^{2}P) + H(^{2}S) + O(^{3}P)$, or -174.5561 hartree (see Table II). The values of θ chosen were 0, 30, 35, 37.5, 40, 42.5, 45, 47.5, 50, 55, 60, 90°, giving a fine grid in the region of the transition state. Again values of l were chosen such that energies up to 1.5 eV above the minimum in each Morse curve were obtained. An abbreviated list of the results is given in Table IV, where we also include (in brackets) the rms error from the least squares fit obtained for D, β , and l_e at each θ . Except for one point at $\theta = 45^\circ$, the rms deviation between F-CI values and the fitted Morse function is less than 0.02 eV. The transition state occurs near $\theta = 47.5^{\circ}$; in Table IV it can be seen that D $=2.92\pm0.01$ eV, where the reported error is that arising solely from the data fit (and not the MRD-CI extrapolation).

Plots of D, β , and l_e vs θ are shown in Fig. 7. The spline fits for D and l_e [Figs. 7(a) and 7(c)] are smooth, whereas the β plot shows some structure near $\theta = 50^{\circ}$. The latter is probably real since the standard error in β is small at that point (see Table IV). The ³II surface derived from the spline functions is shown in Fig. 8. The surface is satisfactory and shows a barrier near

TABLE IV. Quality of the RMCS fits to the ${}^{3}\Pi$ surface, using the 4-31 G basis set. Error estimates for each parameter are as shown in brackets.

θ	No. of points	rms deviation (eV)	D(eV) ²	$\beta(a_0^{-1})$	$_{e}(a_{0})$
0	4	0.005	4.595(0.005)	1.226(0.005)	8,215(0,001)
30	5	0.015	4.614(0.012)	1,087(0,007)	9.482(0.002)
45	4	0.040	3.017(0.040)	0.929(0.040)	11.021(0.014)
47.5	5	0.011	2.916(0.010)	0.991(0.015)	10,860(0,005)
50	4	0.0002	3.177(0.000)	1.088(0.001)	10.562(0.000)
60	4	0.005	3.387(0.002)	1,131(0,002)	9, 391(0, 001)
90	4	0.009	3.397(0.010)	1,291(0,010)	8, 127(0, 002)

^aRelative to the F-CI dissociation limit of -174,5561 hartree.



FIG. 7. RMCS plots for ${}^{3}\Pi$ surface, as in Fig. 4.

 $\theta = 47.5^{\circ}$. From Fig. 7(a), we obtain a barrier height of (3.40 - 2.90) = 0.50 eV, or 11.5 kcal mol⁻¹.

2. ${}^{3}\Pi$, DZP basis. In order to establish a more accurate barrier height, and to imporve the thermochemistry, the DZP basis was used. The oxygen and fluorine 1s orbitals were kept frozen in the CI. Calculations with this basis set were done only for $\theta = 0, 45, 47, 5,$ 50, and 90°, which serves to define reactants, transition state, and products. Atomic energies were also recalculated. Selected results from these calculations are shown in Table V. This table also shows some important features of the MRD-CI calculation. The number of reference configurations needed in the CI step are shown in column 6. The atoms are well described by a single configuration, but three configurations are needed near the transition state. Column 7 lists the number of configurations selected for the CI (at the 50 μ hartree level) versus the total number generated (up to 43 667). There is a large increase in the number of generated configurations as more reference configurations are included, but the selection threshold restricts the dimension of the matrix diagonalization problem to a maximum of 1407. Column 9 shows the error estimate for the MRD-CI extrapolation. The extrapolation error is largest near the transition state, reaching a maximum of 2.2 kcal/mol. This respresents a major source of scatter in the RMCS fit, and is typically worst near the transition state, where both bonds are stretched. The last column shows that the quadruple excitation correction to the MRD-CI eigenvalue typically lowers the energy by 0.02 hartree. The F-CI energy of the swing point is -99.5294 - 74.9166 - 0.4993 = -174.9453hartree.

Using four points at each θ (in addition to the swing point), RMCS fits were obtained and the quality of the fit is shown in Table VI. In order to estimate proper-



FIG. 8. RMCS potential surface for ${}^{3}\Pi$ state with geometry $F \cdots H \cdots O$. The outer contour is at -1.7 eV relative to $F + H + O({}^{3}P)$, contour spacing is 0.4 eV.

Species	θ	R _{OH}	R _{HF}	SC F	No. Main	Select/gener.	MRD-CI	MRD–CI error est.	F–CI
$F(^2P)$	•••		• • •	- 99.3943	1	409/409	- 99, 5253	(0.0000)	- 99, 5294
O(³ P)	•••	•••	•••	- 74.8006	1	442/442	- 74, 9128	(0,0000)	- 74, 9166
H(² S)	•••	•••	• • •	-0.4993	1	• • •	-0,4993	(0.0000)	-0.4993
FHO	0	10,00	1.800	- 174, 8429	2	1027/32608	- 175, 1288	(0.0008)	- 175.1475
FHO	45	2,1511	2,1511	- 174.7568	3	1394/43667	- 175, 0651	(0,0027)	- 175, 0872
FHO	47.5	1.964	2.636	- 174. 7699	3	1407/43667	- 175, 0553	(0, 0035)	- 175, 0753
FHO	50	1.957	3, 251	- 174. 7885	3	1182/43667	-175,0635	(0,0025)	- 175.0818
FHO	90	1,800	10.00	- 174, 7982	2	822/27910	-175.0742	(0.0007)	- 175, 0931

TABLE V. Selected calculations for the ${}^{3}\Pi$ surface using the double-zeta + polarization basis set. Distances are in bohr, energies in hartree.

ties of the transition state, a parabola was passed through the data at 45, 47.5, and 50°. The transition state occurs at $\theta = 47.8^{\circ}$, where $D = 3.52 \pm 0.02$ eV. The results from both basis sets are collected in Table VII for $\theta = 90$ (F + OH, optimum R_{OH}), $\theta = 0$ (HF + O(³P), optimum R_{HF}) and the transition state. These results are used to obtain the reaction energetics. The OH and HF bond strengths are ~74% of the experimental value using the 4-31 G basis and ~89% using the DZP basis. The excergicity is much improved at the DZP level, giving -33.6 kcal/mol compared to the experimental value of -35.1 kcal/mol. This lends confidence in the accuracy of the DZP results. Finally, the energy barrier is found to be 12.4 kcal/mol at the DZP level, compared to 11.5 kcal/mol at the 4-31 G level. This good agreement between barrier height (and barrier location) implies that the shape provided by the 4-31 G basis is qualitatively correct. The computed equilibrium bond distances are also available from Table VI, giving $R_{OH} = (10.8 - 8.141)a_0 = 0.984 \text{ Å and } R_{HF} = (10.0 - 8.245)a_0$ = 0.929 Å. These agree fairly well with the experimental values²⁴ of 0.971 and 0.917 Å, respectively.

3. ${}^{3}\Sigma^{-}$, 4-31 *G* basis. The last surface of interest is the ${}^{3}\Sigma^{-}$ surface, arising from the linear $F \cdots H \cdots O$ geometry with eight sigma and six pi-electrons. This surface could have a lower barrier height than the ${}^{3}\Pi$ surface because of reduced antibonding character near the transition state. Severe convergence difficulties were encountered near the transition state for this state at the SCF stage of the calculation. However, convergence was satisfactory at $\theta = 45^{\circ}$. Since the fitted Morse curves at each θ give a well depth which must lie on the minimum energy path to products, the true barrier must be at least as high as the value derived from the result of 45°. The F-CI result at $\theta = 45^{\circ}$ gave D = 2.96eV, $\beta = 0.91a_{0}^{-1}$, $l_{e} = 10.898a_{0}$. These RMC parameters are similar to those given in Table IV for the ${}^{3}\Pi$ state, where we obtained D=3.02 eV, $\beta=0.93a_{0}^{-1}$, $l_{e}=11.021a_{0}$. The smaller well depth for ${}^{3}\Sigma^{-}$ means a higher energy, so that the ${}^{3}\Sigma^{-}$ barrier height is at least (3.40-2.96)=10.1 kcal mol⁻¹, and probably several kcal mol⁻¹ higher if the transition state does not occur at $\theta=45^{\circ}$. (It should not, since the OH bond is longer than the HF bond for the diatomics.)

VI. DISCUSSION

A plot of the potential energy variation with θ for the various states is shown in Fig. 9. The energies are based on the DZP results, augmented by the 4-31 G estimates of barrier heights, and the known thermochemistry. The nonlinear ¹A' state, which must change geometry from (bent) FOH to $F \cdots H \cdots O$ in order to form products, correlates with $HF + O({}^{1}D)$. A surface crossing occurs late along the reaction coordinate as shown.

The energy at the crossing between ${}^{1}A'$ and ${}^{3}\Pi$ surfaces is not known, but is likely to be lower than that of the reactants. In this event, the only reaction path consistent with both the experimental data and the computed surfaces is that via the bound ${}^{1}A'$ surface, followed by rearrangement and a nonadiabatic transition to the ${}^{3}\Pi$ or ${}^{3}\Sigma^{-}$ surface. In view of the required rearrangement, and of the likely existence of an exit channel barrier, it would be expected that a long-lived intermediate should be involved in this process.

In the event of a very long-lived intermediate, the population of the HF vibrational levels would decrease³¹ as $(1-f'_v)^{3/2}$. The decline shown for v' = 2 and v' = 3 in Fig. 3 appears to be consistent with this, although no firm conclusion can be drawn from only two points. The rotational distributions shown in Fig. 1 are con-

TABLE VI. RMCS fits for the ³	I surface	using the	DZP	basis	set.
--	-----------	-----------	-----	-------	------

θ	<i>D</i> (eV)	$\beta(a_0^{-1})$	$l_{e}(a_{0})$	rms deviation (eV)	max deviation (eV)	Range (eV)
0	5,510(0,008)	1,261(0,011)	8,245(0,002)	0.007	0.012	1.0
45	3.884(0.015)	1,040(0,018)	11.145(0.004)	0.015	0.024	0.62
47.5	3, 521(0, 016)	1.099(0.027)	10,927(0,008)	0.045	0,025	0.88
50	3.734(0.005)	1,016(0,013)	10,563(0,003)	0.005	0.008	0.50
90	4.053(0.904)	1.297(0.005)	8.141(0.001)	0.004	0.007	0.74

This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP:

TABLE VII. Computed thermochemistry for F-CI calculations using both basis sets.

Species	4–31 G (eV)	DZ P (eV)	expt. (eV)
OH(² Π) HF(¹ Σ ⁺) T.S.	3.397 4.595 2.916	4.053 5.510 3.516	4.621 6.123
$F+OH \rightarrow HF+O(^{3}P)$ F+OH $\rightarrow T.S.$	-1.198 0.481	-1.457 0.537	- 1.522ª

^aCorrected for difference in zero-point energy.

sistent with this interpretation as well. A long-lived intermediate of the kind described would produce a rotational distribution which is the same as that of microcanonical ensemble of rotators having the fixed maximum energy (E'_{tot}) indicated earlier. The dashed curves in the upper two panels of Fig. 2 show these statistical rotational distributions for the present system. The close fit with the experimental data suggest that these rotational distributions may indeed originate in the decomposition of a long-lived complex. These data further indicate that the HF v'=2 and v'=3 products have suffered negligible collisional thermalization, since no Boltzmann peak is found in the lower J' states in these cases. The latter point indicated that the v'=2and v'=3 products were formed (on the average) in a lower pressure region than the v'=1 products, and it also suggests a caveat with respect to the interpretation of the vibrational data in Fig. 3. The absence of detectable rotational deactivation in the HF v'=2 and v'=3distributions leaves no way to prove that these molecules have been translationally thermalized before leaving the observation region. (Note that this is not the case with the HF (v'=1) rotational distribution, as discussed earlier.) In the event of incomplete translational thermalization, the apparent P(v'=2)/P(v'=3)will be too low due to the higher velocity of the HF (v'= 2) molecules through the observation region. In view of this, the indicated v'=2 to v'=3 population ratio must be taken as a lower limit.

We note here that the $O({}^{1}D) + H_{2}$ reaction to produce OH (${}^{2}\Pi$) + H (${}^{2}S$) led to very nonstatistical OH rotational populations, 4,5 even though the insertion mechanism was shown by trajectory calculations⁶⁻⁸ to lead to formation of a relatively long-lived complex. In the insertion mechanism as O attacks the H-H bond an excited bending vibration is not fully randomized, but converts into product rotation. In our own case we have a different path, where FOH complex formation is followed by hydrogen migration, and different dynamics will result. It will be of considerable interest to model these migration dynamics on a realistic potential surface, and we expect the exit-channel barrier created by the surface crossing to play a role here.

If surface crossing does occur late along the reaction coordinate, the exit-channel behavior would resemble the conversion of $O(^{1}D)$ to $O(^{3}P)$ by collision with the HF molecule. In fact, the quenching of $O(^{1}D)$ on collision with polar molecules is very efficient, requiring only an average of 1-2 collisions.³² This will occur under the conditions of the experiment, so that the spin forbidden nature of the reaction appears to pose no essential problem. Indeed, new experimental results on a variety of atom-diatom reaction show that singlettriplet transitions do occur frequently.³³⁻³⁶

It is important to consider whether the barrier heights are artificially large due to deficiencies in the calculation. The agreement between split-valence and DZP basis sets is encouraging. However, HML^{26} pointed out that some excited surfaces for H₂O show Rydberg character, and they included additional Rydberg orbitals in their basis set to allow for this possibility. We did not do this, but it seems unlikely that their addition would cause the triplet barriers to drop from the computed 12 kcal mol⁻¹ to the 2–3 kcal mol⁻¹ required to follow the triplet abstraction path.

Another source of uncertainty is our assumption that the lowest triplet barriers lie on a linear reaction path. We have not explored all three bent triplet surfaces $({}^{3}\Pi - {}^{3}A' + {}^{3}A'', {}^{3}\Sigma^{-} - {}^{3}A'')$ to test this assumption. This would be a formidable computational task and is beyond the limit of our present resources. The arguments given earlier, however, using the analogy to the O $({}^{3}P)$ + H₂ reaction, lead us to believe that we have considered the optimum choice of reaction paths.

VII. CONCLUSIONS

The secondary reaction F + OH - HF + O has been observed, arising from the primary reaction $F + H_2O$ -HF+OH. The $F + H_2O$ reaction can populate levels v' = 0 and 1 only, whereas F + OH populates up to v' = 3. The observed emission from v' = 2 and 3 proves that HF is produced from the secondary reaction and that oxygen is in the ground $({}^{3}P)$ state. The HF product from the secondary reaction has a nearly statistical distribu-



FIG. 9. Final potential energy diagram for $F(^{2}P) + OH(^{2}\Pi) \rightarrow HF(^{1}\Sigma^{*}) + O(^{3}P, ^{1}D)$.

tion of vibrational and rotational levels for $v' \ge 2$. Calculation of potential surfaces by the RMCS-CI method shows that the probable route to ground-state products is via the HOF complex. A rearrangement to HF + O (³P) then requires a singlet-triplet surface crossing, which creates an exit-channel barrier. This transition can occur with reasonable probability. The deep potential well and exit channel barrier allow the complex to have a sufficiently long life to account for the observed statistical product, v', J' distributions.

ACKNOWLEDGMENTS

1200

The authors thank R. J. Buenker for the use of his MRD-CI program and the University of Ottawa for a grant of computer time. This work was supported in part by the Natural Sciences and Engineering Research Council of Canada (J. S. W.).

- ¹D. Bogan and D. W. Setser, ACS Symp. Series 66, 237 (1978).
 ²R. G. Macdonald and J. J. Sloan, Chem. Phys. 31, 165 (1978).
- ³J. J. Sloan, D. G. Watson, and J. S. Wright, Chem. Phys. **43**, 1 (1979).
- ⁴G. K. Smith and J. E. Butler, J. Chem. Phys. **75**, 2243 (1980).
- ⁵A. C. Luntz, R. Schinke, W. A. Lester, Jr. and Hs. H. Gunthard, J. Chem. Phys. 70, 5908 (1979).
- ⁶P. A. Whitlock, J. T. Muckerman, and E. R. Fisher, Research Institute for Engineering Sciences Report, Wayne State University (Nov. 1976).
- ⁷K. S. Sorbie and J. N. Murrell, Mol. Phys. **31**, 905 (1976).
- ⁸R. Schinke and W. A. Lester, Jr., J. Chem. Phys. 72, 3754 (1980).
- ⁹D. J. Douglas, J. C. Polanyi, and J. J. Sloan, Chem. Phys. 13, 15 (1976).
- ¹⁰(a) K. G. Anlauf, D. H. Maylotte, J. C. Polanyi, and R. B. Bernstein, J. Chem. Phys. **51**, 5716 (1969); (b) J. C. Polanyi, and D. C. Tardy, J. Chem. Phys. **51**, 5717 (1969).
- ¹¹K. P. Huber and G. Herzberg, Molecular Spectra and Molecular Structure. IV. Constants of Diatomic Molecules (Van Nostrand, New York, 1979).
- ¹²(a) F. H. Mies, J. Mol. Spectrosc. **53**, 150 (1974); (b) J. M. Herbelin and G. Emanuel, J. Chem. Phys. **60**, 689 (1974).
- ¹³(a) A. B. Callear, in "Gas Kinetics and Energy Transfer (The Chemical Society, London, 1978), Vol. 3; (b) R. T. Bailey

and F. R. Cruickshank, ibid.

- ¹⁴A. M. G. Ding, L. J. Kirsch, D. S. Perry, J. C. Polanyi, and J. L. Schreiber, Faraday Discuss. Chem. Soc. 55, 252 (1973).
- ¹⁵(a) R. J. Buenker and S. D. Peyerimhoff, Theor. Chim. Acta **35**, 33 (1974); (b) **39**, 217 (1975).
- ¹⁶R. J. Buenker, S. D. Peyerimhoff, and W. Butscher, Mol. Phys. **35**, 771 (1978).
- ¹⁷E. R. Davidson, in *The World of Quantum Chemistry*, edited by R. Daudel and B. Pullman (Reidel, Dordrecht, Holland, 1974), p. 17.
- ¹⁸W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton, and J. A. Pople, QCPE **11**, 236 (1973).
- ¹⁹R. J. Ditchfield, W. J. Hehre, and J. A. Pople, J. Chem. Phys. **54**, 724 (1971).
- ²⁰S. Huzinaga, J. Chem. Phys. 42, 1293 (1965).
- ²¹(a) T. H. Dunning, Jr., J. Chem. Phys. 53, 2823 (1970);
 (b) T. H. Dunning, Jr. and P. J. Hay, in *Methods of Electronic Structure Theory*, edited by H. F. Schaefer III (Plenum, New York, 1977), p. 1.
- ²²J. S. Wright and S. K. Gray, J. Chem. Phys. **69**, 67 (1978) and references therein.
- ²³J. S. Wright and S. K. Shih, J. Chem. Phys. 73, 5204 (1980).
- ²⁴G. Herzberg, Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules (Van Nostrand, New York, 1950), p. 447.
- ²⁵M. C. Addison, R. J. Donovan, and D. Husain, Chem. Phys. Lett. 44, 602 (1976).
- ²⁶R. E. Howard, A. D. McLean, and W. A. Lester, Jr., J. Chem. Phys. 71, 2412 (1979).
- ²⁷E. F. Pearson and H. Kim, J. Chem. Phys. 57, 4230 (1972).
- ²⁸H. Kim and J. R. Sabin, Chem. Phys. Lett. 20, 215 (1973).
 ²⁹R. J. Buenker and S. D. Peyerimhoff, J. Chem. Phys. 45,
- 3682 (1966).
- ³⁰S. P. Walch, T. H. Dunning, Jr., F. W. Bobrowicz, and R. C. Raffeneti, J. Chem. Phys. **72**, 406 (1980).
- ³¹R. D. Levine and J. L. Kinsey in Atom-Molecule Collision Theory—A Guide for the Experimentalist, edited by R. B. Bernstein (Plenum, New York, 1979).
- ³²M. J. E. Gauthier and D. R. Snelling, J. Photochem. 4, 27 (1975).
- ³³C. F. Carter, M. R. Levy, K. B. Woodall, and R. Grice, Farad. Discuss. Chem. Soc. **55**, 381 (1973).
- ³⁴D. A. Dixon, D. D. Parrish, and D. R. Herschbach, Farad. Discuss. Chem. Soc. 55, 385 (1973).
- ³⁵D. L. King and D. W. Setser, Annu. Rev. Phys. Chem. 27, 407 (1976).
- ³⁶J. Troe, Annu. Rev. Phys. Chem. 29, 223 (1978).