Title
HYDROXYL RADICAL KINETICS: REACTION WITH OZONE AND VIBRATIONAL QUENCHING

Permalink
https://escholarship.org/uc/item/2528k58v

Author
Streit, Gerald E.

Publication Date
1974-08-23
HYDROXYL RADICAL KINETICS: REACTION WITH OZONE AND VIBRATIONAL QUENCHING

Gerald E. Streit
(Ph.D. thesis)

August 23, 1974

Prepared for the U. S. Atomic Energy Commission under Contract W-7405-ENG-48

TWO-WEEK LOAN COPY
This is a Library Circulating Copy which may be borrowed for two weeks. For a personal retention copy, call Tech. Info. Division, Ext. 5545
DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.
Table of Contents

ABSTRACT ................................................................. v
I. INTRODUCTION ....................................................... 1
II. EXPERIMENTAL ........................................................ 5
   A. Apparatus .......................................................... 5
   B. Procedure ......................................................... 14
III. TECHNIQUES OF EXPERIMENTAL ANALYSIS ................. 17
   A. Basic Spectroscopy of the Hydroxyl Radical ............... 19
   B. Determination of Vibrational Populations ................. 26
      1. Intensity of a Line in Emission ......................... 26
      2. Transition Probabilities ................................. 29
      3. Details of Calculation of Synthetic Spectrum .......... 34
      4. Population Fitting and Rotational Temperatures ....... 38
   C. Determination of Kinetic Rate Constants .................. 47
      1. Mechanism of the Hydroxyl Radical System .............. 50
      2. Computational Model of the Hydroxyl Radical System . 54
IV. RESULTS AND DISCUSSION ......................................... 60
   A. Initial Vibrational Population Distributions and
      Vibrational Temperature ........................................ 60
   B. Determination of the Wall Quenching Constant ............ 67
   C. Rotational Temperature ........................................ 68
   D. Reaction Rate Constants for Hydroxyl Plus Ozone .......... 71
   E. Results for Quenching HO(v), v=4-9 ......................... 80
      1. Quenching with Argon ..................................... 82
      2. Quenching with Oxygen .................................... 82
3. Quenching with Nitrogen .......... 87
4. Quenching with Hydrogen .......... 87
5. Quenching with Deuterium .......... 94

V. VIBRATIONAL ENERGY TRANSFER ................. 97
   A. Review of Selected Energy Transfer Theories and
      Experiments .................................. 97
      1. V-T Energy Transfer ....................... 98
      2. V-V Energy Transfer ....................... 101
   B. Energy Transfer in Vibrationally Excited HO .......... 107

ACKNOWLEDGEMENTS ....................... 113

APPENDICES ....................... 114
   I. Computer Programs ....................... 114
   II. Error Analysis .......................... 131
   III. Models for Hydroxyl Radicals in the Stratosphere .. 135

REFERENCES ....................... 144
HYDROXYL RADICAL KINETICS: 
REACTION WITH OZONE AND VIBRATIONAL QUENCHING

Gerald E. Streit

Inorganic Materials Research Division, Lawrence Berkeley Laboratory and 
Department of Chemistry; University of California, 
Berkeley, California

ABSTRACT

Rate constants for the gas phase reaction of vibrationally 
excited hydroxyl radicals (v<9) with ozone and for vibrational 
quenching of hydroxyl radicals by argon, hydrogen, nitrogen, oxygen, 
and deuterium have been measured. The relative rates of formation of 
hydroxyl radicals into each of six vibrational levels has also been 
measured.

The technique used was to measure the pressure dependence of 
hydroxyl radical chemiluminescence emission from the \( \Delta v=4,5, \) or 6 
overtones bands in the wavelength region 5500Å to 8500Å. Vibrational 
populations were derived from the emission spectra by finding the set 
of populations which gave the best fit between an observed spectrum 
and a synthetically calculated spectrum. Rate constants were derived 
by interpreting the dependence of vibrational populations on reactant 
pressure in terms of a comprehensive model of the hydroxyl system. 
The model restricted vibrational quenching to single quantum steps.

Rate constants for the hydroxyl reaction with ozone were found to 
be highly dependent on the hydroxyl vibrational level and to be a 
lesser function of the number of product channels available. Vibrational 
quenching constants were found to be a complex function of vibrational 
level, exhibiting a maximum at \( v=6 \) or 7.
Possible energy transfer mechanisms are discussed with the general conclusion that HO is efficiently quenched through weak chemical interactions which allow rotational excitation to absorb most of the vibrational energy defect. The results are also applied to a model calculation of the stratosphere in which it is found that vibrationally excited hydroxyl radicals are rapidly quenched at all altitudes and are not a major factor in daytime chemistry.
I. INTRODUCTION

Vibrationally excited hydroxyl radicals have occupied the interest of many researchers since Meinel first observed hydroxyl emission bands in the night sky airglow.\(^1\) The production of excited hydroxyl radicals is acknowledged to be due to the reaction

\[ \text{H} + \text{O}_3 \rightarrow \text{HO}(v=9) + \text{O}_2 \]  

(1)

which is 77 kcal/mole exothermic. This is just enough to populate up to vibrational level, \(v=9\), of the \(\text{2}\Pi_1\) ground electronic state.

The vibration-rotation emission spectrum of the hydroxyl system has since been studied many times, both by observation of the airglow\(^2-4\) and by observations in the laboratory.\(^5-8\) The intent of these studies, in almost all cases, was to measure or derive the initial vibrational population distribution produced by reaction (1). After considerable disagreement among earlier researchers, there is now substantial agreement that the population distribution is close to that reported by Polanyi and co-workers.\(^8\)

However, there has been very little study of the reactions of vibrationally excited hydroxyl. This is primarily due to the complexity of a multi-state system in which each vibrational state is linked to the others by radiative or collisional transitions. Worley and co-workers\(^9,10\) have reported rate constants for the following reactions.

\[ \text{HO}(2<v<9) + \text{O}_3 \rightarrow \text{products} \]  

(2)

\[ \text{HO}(v=9) + \text{M} \rightarrow \text{HO}(v<9) + \text{M} \text{ (10 different M)} \]  

(3)
They observed the time dependent decay, in a fast flow tube, of the \( \Delta v=2 \) overtone emission bands in the infrared. By integrating only over non-overlapping portions of the bands, they were able to obtain vibrational populations directly, and from those calculate rate constants.

There are several reasons for which the reactions of vibrationally excited hydroxyl radicals are of interest. There has recently been a great increase in effort applied to discovering and understanding the chemistry of the upper atmosphere. Because the chemistry of the stratosphere is almost exclusively the chemistry of free radicals and because hydroxyl is a vital part of the \( \text{HO} \) system, it becomes important to determine the significance of vibrationally excited hydroxyls in the stratosphere.

From a more general point of view, the fact that reaction (1) produces an entire manifold of vibrational states provides the opportunity to study the dependence of a reaction rate constant on the level of excitation of one of the reaction partners. This may give some insight into the potential surface on which the reaction takes place and in particular may point to the specific reaction channel which is followed. Finally there is the opportunity to do a quantum resolved study of energy transfer with a molecule containing many quanta of vibrational energy in the ground electronic state. Energy transfer processes in highly excited molecules are responsible either for the decomposition or the stabilization of products of a chemical reaction, yet very little is known about these processes. Further, energy transfer rates and
the dependence of those rates on vibrational quantum number may reveal the nature of the interaction between two colliding molecules. The nature of the interaction, whether through short range repulsive forces, through long range attractive forces, or through chemical forces, is, to a simple approximation, expected to be mirrored in the rate of the energy transfer process.

In this work, chemiluminescence emission from vibrationally excited hydroxyl radicals was observed at low pressure in the spectral region 5500Å - 8500Å. Emission in this region is from the Δν=4,5,6 overtone bands. Because there is considerable overlapping of the bands in this region, vibrational populations were obtained by finding the set of populations which gave the best fit between a synthetic computed spectrum and an observed spectrum.

Rate constants were determined by measuring the pressure dependent behavior of emission intensity. By observing intensity of ten different peaks in the hydroxyl spectrum as the concentration of a reactant was slowly increased and calculating populations from those intensities, a complete set of populations versus pressure data could be obtained for the six vibrational levels studied in this work. This data was then interpreted to find rate constants by fitting it to a comprehensive model of the system. In this manner rate constants for reaction with ozone and for vibrational quenching by argon, hydrogen, deuterium, nitrogen, and oxygen were obtained.

The theories of energy transfer for vibration-translation and vibration-vibration processes are reviewed and their qualitative predictions are compared to the present results on hydroxyl quenching. There is
very little quantitative theory for energy transfer from high vibrational levels so the results of this work provide an experimental reference for future theory. The rate constants obtained here for reaction with ozone and for quenching by nitrogen and oxygen are also applied to a computer model of the stratosphere to determine the effect, if any, that vibrationally excited hydroxyl radicals have in the chemistry of the stratosphere. Three versions of the chemical model were calculated. One allows only ground state (v=0) hydroxyl radicals to be produced, or in other words vibrationally excited hydroxyls are instantaneously quenched, another allows excited hydroxyls to be produced only by reaction (1), and the third allows every reaction that produces hydroxyl radicals to produce them excited to the very limit of the energetics of the reaction.
II. EXPERIMENTAL

A. Apparatus

The experimental apparatus used in this work is shown schematically in Fig. 1. The apparatus is designed for detection of low level chemiluminescent emission at working pressures as low as $1 \times 10^{-4}$ Torr.

The heart of the system is a 340 liter cigar-shaped stainless steel cell with multiple inlets for gas delivery or pressure measurement. The cell was fitted with 2 in. diameter quartz end windows for chemiluminescence detection which also allowed for single pass absorption measurements with a path length of 139 cm. The cell was pumped through a 7 in. internal diameter gate valve, a liquid nitrogen cold trap, and a chevron type water cooled baffle by a 6 in. oil diffusion pump backed by a 35 CFM rough pump.

Pressure was measured in the system by thermocouple (Hastings Vacuum Gauge Tube DV-3M), ionization gauge (Alfred Ionization Gauge Control Model 101C, Consolidated Vacuum Corporation VG1A/2 tube) or by a capacitance pressure transducer (Datametrics Model 511-10, controller Model 1014). The transducer was used for recording pressure during experiments. The manufacturer stated the linearity of this instrument to be 0.1% over the entire 0-10 Torr range. The most sensitive range was 1 m Torr full scale. The cell was typically pumped to a background pressure of approximately $5 \times 10^{-6}$ Torr before any experiment.
Fig. 1.
Gas handling was done through an all glass vacuum line constructed with greaseless teflon stopcocks. This line was pumped by a 2 in. oil diffusion pump and protected by a water cooled baffle and liquid nitrogen trap. Gas flow rates were measured by use of several Hastings-Raydist Model LF-50 calorimetric mass flowmeters. This was for convenience only because concentrations rather than flow rates were important in this work. Gases were used directly from the cylinder except for the oxygen supplied to the ozonizer which was rigorously prepurified. Gases and their purities are listed in Table I.

The ozone used in this work was prepared by flowing LBL supplied oxygen through an electric discharge ozonizer. The ozone was separated from oxygen by a silica gel trap (6-12 mesh) held at -78°C. Ozone could be stored for long periods of time in this trap. The oxygen was purified by passing it through a glass tube containing copper turnings at 600°C, through a column containing pellets of 0.5% palladium on alumina at 350°C and then through columns of ascarite and phosphoric anhydride (P$_2$O$_5$). During an experiment ozone is desorbed from the silica gel trap and flows into the cell under its own pressure. To further purify the ozone, the trap was usually pumped down to 0.5-1.0 Torr before experiments to remove residual oxygen. At the -78°C trap temperature the partial pressure of ozone is approximately 10 Torr. A complete discussion of separation of ozone by absorption on silica gel and the handling characteristics of the stored ozone has been presented by Cook and co-workers.ii
### Table I. Reagents

<table>
<thead>
<tr>
<th>Gas</th>
<th>Supplier</th>
<th>Minimum Purity</th>
<th>Major Impurity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>Matheson</td>
<td>99.999%</td>
<td></td>
</tr>
<tr>
<td>Deuterium</td>
<td>Liquid Carbonic</td>
<td>99.97 %</td>
<td>H₂</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>Lawrence Berkeley Laboratory</td>
<td>99.999%</td>
<td></td>
</tr>
<tr>
<td>Oxygen</td>
<td>Lawrence Berkeley Laboratory</td>
<td>99.6%</td>
<td>Ar(0.3%)</td>
</tr>
<tr>
<td>Argon</td>
<td>Lawrence Berkeley Laboratory</td>
<td>99.999%</td>
<td></td>
</tr>
</tbody>
</table>
Ozone concentration in the cell was determined by measuring absorption at 2550Å. The source lamp was a Bausch and Lomb Deuterium Light Source, type 33-86-35. The absorption cross section at this wavelength is $1.1193 \times 10^{-17}$ cm$^2$ as determined by Ackerman.\(^{12}\)

Hydrogen atoms were produced by flowing moist hydrogen with a small amount of added argon through a 13 mm o.d. quartz discharge tube placed in a number 5 microwave discharge cavity as described by Broida, et al.\(^{13}\) Moistened hydrogen, bubbled through water at room temperature to attain a water vapor content of 2-3%, has been found to significantly increase H atom production, probably due to a decrease in surface recombination efficiency.\(^{14}\) Though Rony\(^{15}\) vehemently disputes this idea, it was noticed that addition of water helped to stabilize the discharge, so the procedure was continued. The microwave power supply used was a Burdick 2450 MHz diathermy unit.

The monochromator used in the work was a 0.3 meter McPherson scanning monochromator, model 218. This is an f/5.3 instrument and was equipped with a 1200 line/mm grating blazed at 5000Å. Slit height was adjustable, but maintained at 20 mm. The slit opening was adjustable from 10 microns to 2 mm. When determining ozone absorption the slits were set at 100 μ which with this grating gave a resolution of 6Å or 0.6 nm.

When observing NO emission, the slits were opened to 1000 μ. It is very important to know the spectral slit function for interpretation of spectral data. This function is needed to compute the response of the entire detection system to an emission line with
a Doppler width narrower than the operating resolution of the monochromator. To determine this function, the monochromator was scanned very slowly (to avoid effects of RC time constant) over an isolated atomic line. A typical response is shown in Fig. 2. In calculations the slit function has been approximated by a triangular function with full width at half maximum of 26.2 Å. This is very close to the 26.5 Å/mm dispersion stated by the manufacturer.

An EMI 9558QA photomultiplier tube with an S-20 type spectral response and a quartz window was used as an optical detector. The high voltage power supply was a Fluke, model 412B, with stability within .005% per hour and less than 1 mv peak to peak ripple. The signal from the phototube was converted to uniform pulses by a high gain amplifier/discriminator (Solid State Radiation model 1120) specifically designed for photon counting. The amplifier/discriminator output was received by the SSR model 1105 Data Converter Console which included precision linear ratemeters and output terminals for taking off digital or analog signals.

When scanning the hydroxyl spectrum, the analog signal was fed into a Fabri-Tek model 1074 signal averager for further processing by a laboratory PDP-8 computer or to be punched on paper tape for processing on a CDC 7600 computer. When doing an intensity vs. pressure experiment the analog signals from the ratemeter and from the pressure transducer were digitized by a Preston model 723A digital voltmeter interfaced to a paper tape punch where the information was output on alternate channels.
The operation and detection statistics of the photomultiplier tube deserve further discussion. Because this tube is a red sensitive tube with a large cathode area (44 mm diameter), dark current from several sources is a significant problem. First there is statistical thermal noise due to the low work function of the photocathode surface. There is also thermal noise due to the dynode chain, but this is expected to be small because the work function of the dynodes is much higher. Thirdly there is significant non-statistical noise due to cosmic rays or other uncontrollable sources.\textsuperscript{16}

Several techniques and precautions were used to manage these problems. Photon counting was used so that high intensity bursts are counted as equivalent to signal photons rather than giving rise to a very large signal as would occur in an analog voltage measuring system. The discriminator was set at a level of 50 \( \mu \)V, i.e. pulses of lower intensity were not counted. The tube was operated with grounded cathode and the anode at +1210 volts. This low voltage optimized the gain at approximately \( 10^6 \), and was determined by the procedure described in the SSR Photon Counter operating manual.\textsuperscript{17} The cathode was grounded so the dynode chain might be optimumly wired for photon counting and so that shielding might also be held at ground potential.

The tube was cooled to approximately \(-60^\circ\text{C}\) by cold \( \text{N}_2 \) gas. The phototube housing was designed to incorporate all of the features described in reference 16, including concentric cylinders of Netic and Co-netic metals and an additional shield of mu-metal. The housing
had double quartz windows between which warmed N₂ gas flowed to prevent fogging and incorporated an option for placement of toroidal defocussing magnets. The magnet used (EMI type MFA) reduced the effective photocathode diameter to 10 mm and reduced dark current to 9% of that with no magnet.

In operation the phototube dark current was 10-15 counts/sec and though this dark current maintained a non-statistical nature (statistical standard deviation = 3.5 counts/sec, measured standard deviation = 7 counts/sec), it was sufficiently reduced below signal level to pose no further problem.

The spectral response of the entire detection system must also be determined so measured spectral intensities may be corrected to true intensities. For this purpose a General Electric 30A/T24/17 tungsten ribbon lamp was used as a black body source (after appropriate corections). The lamp's power supply was photo-regulated as described by Gabelnick [18] and the brightness temperature of the lamp was measured by a Leeds and Northrup Model 8622-C optical pyrometer which was calibrated at the Lawrence Berkeley Laboratory.

For a true blackbody, the Planck radiation distribution law is,

\[ I_{\lambda T} d\lambda = \frac{8\pi}{\lambda^4} \frac{d\lambda}{(e^{hc/kT} - 1)} \]  

However a tungsten ribbon has an emissivity, E(λ, T), which is defined as the ratio of emission of tungsten to the emission of a true blackbody, both at the same λ and T. Emissivities for tungsten are
given by DeVos. Including emissivity and converting Eq. (1) to wavelength in Angstroms we have

\[ I_{\lambda T}d\lambda = \frac{8\pi \times 10^{32}}{\lambda^4} \frac{E(\lambda, T)d\lambda}{[\exp(10^8 hc/kT)-1]} \]

(2)

Spectral response corrections are obtained by dividing the true spectrum calculated from Eq. (2) by the observed spectrum.

With a lamp brightness temperature of 1725°K and a true temperature of 1855°K (see Ref. 20 for conversion scale), the spectrum was slowly scanned from 4900 Å to 8500 Å. The calculations were carried out on the CDC 7600 computer and the correction curve, normalized to 5000 Å, is shown in Fig. 3.

B. Procedure

Before any set of experiments involving the same reactant or gas, the cell and all gas delivery lines were baked (250°C) and pumped for at least 3-5 days to below 1×10^-5 Torr, usually to about 5×10^-6 Torr. Between related experiments, the cell was baked and pumped overnight.

All electronics and the microwave discharge were warmed up and allowed to stabilize for one hour before experimentation. Hydrogen flows through the discharge were typically 1-3 cm^3/min (0.8-2.5 μmoles/sec). With the added argon needed to maintain the discharge, the resultant cell pressure was 4×10^-4 Torr. Ozone was added until total background pressure before addition of any further reactant or quenching gas was 0.8-1.0×10^-3 Torr.
Fig. 3. Spectral Sensitivity Correction Curve.
Data could be gathered by two different methods. The spectrum could be scanned from 5500 Å to 8500 Å at constant pressure. This spectrum involves 11 bands of hydroxyl overtone emission. The pressure of reactant or M gas might then be changed and another spectrum recorded. This technique was good for obtaining low pressure spectral information, rotational temperatures and very fast reaction rate constants (i.e. HO(v) + O3). However due to serious pumping instability, it was impossible to maintain constant high pressure during a scan, so this method was inadequate to obtain quenching rate constants.

The second method was to observe changes in emission intensity of selected lines from the hydroxyl spectrum while pressure of the reactant or quenching gas was slowly increased. This procedure proved far more satisfactory because it yields continuous pressure dependent data rather than the continuous wavelength dependent data of a spectral scan. The output from the SSR ratemeter and the Datametrics pressure transducer were fed into the two channels of a digital voltmeter - paper tape punch interface and punched periodically by a line frequency dependent interrupt system. Periods were typically 4 seconds and maximum pressure about 0.1 Torr (100 microns). This data was then in convenient form for later computer calculations.
III. TECHNIQUES OF EXPERIMENTAL ANALYSIS

The experimental problem undertaken here involves three major parts: 1) Observation and recording of hydroxyl emission under a suitable variety of conditions, 2) Interpretation of these emission signals to yield sets of stationary state vibrational populations, \( N_v \), and a set of fractions describing the relative initial vibrational distribution, \( f_v \), and 3) Interpretation of the initial vibrational distribution and subsequent population distributions by some kinetic model to yield reaction or quenching rate constants. The first part was discussed in the previous section, the next two parts will be discussed in the several following subsections.

Of primary importance in attempting to do a quantum resolved kinetics experiment is to resolve successfully the separate vibrational populations from the emission spectrum. In a spectrum with non-overlapping bands, this is easy, merely integrate the intensity under each band and apply appropriate detection and transition probability corrections. Unfortunately few molecules qualify under the totally separated band restriction, and we find that we must determine populations from overlapping bands. Several techniques have been devised to accomplish this, among them being the Fractional Band Intensity Method and the Rotational Line Intensity Method. The first measures some fraction of the band, such as the band head, and relates it to the intensity of the entire band. The striking assumption is that the band head intensity remains a constant fraction of the total band.
intensity. In chemically produced systems vibrational and rotational populations are often found to be non-Boltzmann at low pressure, and the shift in populations as the system becomes Boltzmann would invalidate this assumption. The Rotational Line Intensity Method is based on measuring the intensity of a few well resolved lines and inferring from that the intensity of the entire band. In this experiment, such resolution was not possible, but the method also fails on the same assumption of Boltzmann populations. A complete discussion of these methods and where they are applicable is presented by Robinson and Nicholls. 21

The technique used here is similar to that used by Gabelnick 18 for the IF molecule and by Smith 22 for the CO molecule. This method involves computing a synthetic spectrum using the known spectroscopic quantities for hydroxyl and then correcting for the spectral slit function, detector response, and the RC time constant of the detection system. The synthetic spectrum is then fitted to the observed spectrum by varying a proposed set of vibrational populations until the best fit is obtained. The vibrational temperature of the system is not involved, rather it may be calculated from the final set of N_v. However an estimate for a Boltzmann rotational temperature is involved, and the uncertainties accompanying this estimate will be discussed in a later section.

It is first necessary to assemble a complete spectroscopic description of the hydroxyl radical.
A. Basic Spectroscopy of the Hydroxyl Radical

Ground state hydroxyl is in a $^2\Pi$ electronic state, thus designating the quantum number $\Lambda=1$. The quantum number $\Lambda = |M_L|$ where $M_L$ is the component of the electronic angular momentum directed along the internuclear axis. The hydroxyl radical, having an odd number of electrons, has a resultant spin quantum number $S=1/2$. The component of $S$ along the internuclear axis is designated $\Sigma$ and for hydroxyl has the value $\pm 1/2$. Finally we have the resultant of the total electronic angular momentum about the internuclear axis which is

$$\Omega = |\Lambda + \Sigma| .$$

The various angular momenta in the molecule; spin, orbital, and nuclear, always interact, or couple, to form a resultant designated $J$. However there are different manners of coupling these momenta and these cases have been distinguished by Hund. See Herzberg\textsuperscript{23} for a full discussion of Hund's coupling cases. The hydroxyl radical has been designated as intermediate between Hund's cases a and b, so we shall briefly examine those two cases.

In Hund's case a the interaction of nuclear rotation with electronic motion is considered weak, whereas the electronic motion is strongly coupled to the internuclear axis. Rotation is slow enough that this coupling is not disturbed. Rotational energy is approximately $BJ(J+1)$ where $J$ is the total angular momentum. In Hund's case b, common for light molecules, the rotation is so strong that the spin is coupled to the rotational axis rather than the
internuclear axis. A new quantum number $K$ is created which is the resultant of $A$ and $N$, or of the internuclear axis and the nuclear angular momentum. $K$ is thus the total angular momentum apart from spin. The total angular momentum including spin is again designated $J$ and is the resultant of $K$ and $S$. For case $b$, $K = 0, 1, 2, \ldots$, and there are two states:

$$F_1(K): J = K + \frac{1}{2} \quad F_2(K): J = K - \frac{1}{2}$$

The rotational energy is given approximately by $B[K(K+1)-\Lambda^2]$.

In a transition from case $a$ to case $b$, the electronic spin $S$ is first coupled with $A$, but as $J$ increase, the rotational velocity of the molecule increases and the influence of molecular rotation becomes predominant. In this situation $S$ uncouples from the molecular axis ($\Lambda$) and forms with $K$ the total angular momentum $J$. This process is called spin uncoupling and is characteristic of the hydroxyl radical.

The hydroxyl radical, being in a $^2\Pi$ electronic state, has two multiplets designated $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$. A rotational level diagram with the most probable transitions is shown in Fig. 4. It may be seen that in hydroxyl emission there are three main branches in each multiplet as a result of the transition selection rule: $J = 0, \pm 1$. These bands, in emission, are characterized as follows:

$$R: J'' = J' - 1 \quad Q: J'' = J' \quad P: J'' = J' + 1$$
Fig. 4. Rotational Structure and Branch Identification of the Two Hydroxyl Multiplets.
following traditional notation that double prime (""") denotes the lower state. There are in addition six satellite branches which involve transitions between the multiplets, but the transition probabilities for these are so low, that their intensity contributions to the hydroxyl emission spectrum are negligible.

The rotational energy must also be intermediate between cases a and b. The term values have been calculated by Hill and Van Vleck\textsuperscript{24} who found that

\[
2\pi_{3/2} F_{1}^{}(J) = B_{v} \left[ (J + \frac{1}{2})^{2} - \Lambda^{2} - \frac{1}{2} \sqrt{4(J + \frac{1}{2})^{2} + Y_{v}^{2}(Y_{v} - 4)\Lambda^{2}} \right] - D_{v} J^{4} \quad (3a)
\]

\[
2\pi_{1/2} F_{2}^{}(J) = B_{v} \left[ (J + \frac{1}{2})^{2} - \Lambda^{2} + \frac{1}{2} \sqrt{4(J + \frac{1}{2})^{2} + Y_{v}^{2}(Y_{v} - 4)\Lambda^{2}} \right] - D_{v} (J+1)^{4} \quad (3b)
\]

where \( Y_{v} = A_{v} / B_{v} \). \( A_{v} \) is the coupling constant which is a measure of the strength of coupling between the spin and the orbital angular momentum.

The vibrational structure of the \( \text{^2}\pi \) ground state up to \( v=9 \) has been well determined by observation of many researchers.\textsuperscript{25-29} The energy of a vibrational level up to \( v=9 \) is given by

\[
G(v) = \omega_{e} (v + \frac{1}{2}) - \omega_{x} x_{e} (v + \frac{1}{2})^{2} + \omega_{y} y_{e} (v + \frac{1}{2})^{3} + \omega_{z} z_{e} (v + \frac{1}{2})^{4} + \ldots \quad (4)
\]

With the best set of molecular constants (Ref. 26), Eq. (4) takes the form
\[ G(v) = \]
\[ 3737.90(v+\frac{1}{2}) - 84.965(v+\frac{1}{2})^2 + 0.5398(v+\frac{1}{2})^3 - 0.01674(v+\frac{1}{2})^4 - 0.001637(v+\frac{1}{2})^5 \]

All coefficients are in units of cm\(^{-1}\). Most commonly the vibrational energy is referred to the energy of \(v=0\) and is given by

\[ G_0(v) = G(v) - G(0) \]

The rotational constant for each vibrational level is given by

\[ B_v = B_e - \alpha_e (v+\frac{1}{2}) + \gamma_e (v+\frac{1}{2})^2 \]

According to Ref. 25, \(B_e = 18.867\) cm\(^{-1}\), \(\alpha_e = 0.708\) cm\(^{-1}\), and \(\gamma_e = 0.00207\) cm\(^{-1}\).

The complete vibrational and rotational structure for HO up to \(v=9\) is given in Table II.

The potential energy curve for the \(2\pi\) ground state has been calculated by Fallon et al.\(^{30}\) by the Rydberg - Klein - Rees method using the spectroscopic data from the literature. Their curve is shown in Fig. 5.

It is now necessary to relate the spectroscopic information to the intensity of emission expected from the hydroxyl radical.
Table II. Rotational and Vibrational Structure of Hydroxyl

<table>
<thead>
<tr>
<th>V</th>
<th>$\frac{B_v}{\text{cm}^{-1}}$</th>
<th>$\frac{A_v}{\text{cm}^{-1}}$</th>
<th>$\frac{D_v}{\text{cm}^{-1}}$</th>
<th>$\frac{Y_v}{\text{cm}^{-1}}$</th>
<th>$\frac{G(v)}{\text{cm}^{-1}}$</th>
<th>$\frac{G_o(v)}{\text{cm}^{-1}}$</th>
<th>$\text{(kcal)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>18.515</td>
<td>-139.7</td>
<td>0.0018</td>
<td>-7.547</td>
<td>1847.78</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>1</td>
<td>17.807</td>
<td>-140.2</td>
<td>0.0018</td>
<td>-7.876</td>
<td>5417.41</td>
<td>3569.63</td>
<td>10.21</td>
</tr>
<tr>
<td>2</td>
<td>17.108</td>
<td>-140.5</td>
<td>0.0018</td>
<td>-8.214</td>
<td>8821.36</td>
<td>6973.58</td>
<td>19.94</td>
</tr>
<tr>
<td>3</td>
<td>16.414</td>
<td>-140.6</td>
<td>0.0018</td>
<td>-8.568</td>
<td>12061.61</td>
<td>10213.83</td>
<td>29.19</td>
</tr>
<tr>
<td>4</td>
<td>15.722</td>
<td>-140.6</td>
<td>0.0018</td>
<td>-8.941</td>
<td>15139.28</td>
<td>13291.50</td>
<td>37.99</td>
</tr>
<tr>
<td>5</td>
<td>15.033</td>
<td>-140.8</td>
<td>0.0018</td>
<td>-9.368</td>
<td>18054.52</td>
<td>16206.74</td>
<td>46.31</td>
</tr>
<tr>
<td>6</td>
<td>14.349</td>
<td>-140.5</td>
<td>0.0018</td>
<td>-9.795</td>
<td>20805.95</td>
<td>18958.17</td>
<td>54.17</td>
</tr>
<tr>
<td>7</td>
<td>13.65</td>
<td>-141.1</td>
<td>0.0018</td>
<td>-10.34</td>
<td>23392.1</td>
<td>21544.3</td>
<td>61.57</td>
</tr>
<tr>
<td>8</td>
<td>12.91</td>
<td>-140.4</td>
<td>0.0018</td>
<td>-10.95</td>
<td>25806.7</td>
<td>23958.9</td>
<td>68.47</td>
</tr>
<tr>
<td>9</td>
<td>12.12</td>
<td>-140.4</td>
<td>0.0018</td>
<td>-11.58</td>
<td>28043.5</td>
<td>26195.7</td>
<td>74.88</td>
</tr>
</tbody>
</table>
Fig. 5. RKR Potential Energy Curve for the Hydroxyl Ground State ($^{2}π$).
B. Determination of Vibrational Populations

1. Intensity of a Line in Emission

The most general relationship for the intensity of a spectral line in emission is given as

\[ I_{nm} = N_n h c \nu_{nm} A_{nm} \]  \hspace{1cm} (7)

where the subscripts \( n \) and \( m \) denote initial and final states respectively, \( N_n \) is the population of the emitting state, \( h c \nu_{nm} \) is the energy of a quanta of light of wave number \( \nu_{nm} \), and \( A_{nm} \) is the Einstein transition probability of spontaneous emission which is defined as

\[ A_{nm} = \frac{64\pi^3 \nu_{nm}^3}{3h} |R_{nm}|^2 \]  \hspace{1cm} (8)

Here \( h \) is Planck's constant and \( R_{nm} \) is the transition matrix element, or transition moment, defined as

\[ R_{nm} = \langle \psi_n | M | \psi_m \rangle \]

where \( M \) is the electric dipole moment.

However, the intensity defined in Eq. (7) is in terms of energy emitted per second. In this system a measure is made of intensity in terms of quanta per second so the following conversion must be made.
quanta/sec = \frac{\text{energy/sec}}{\text{energy/quanta}}

Energy per quanta is, as noted above, $h \nu_{nm}$, so intensity in terms of quanta per second may be written as

$$I_{nm}\text{(quanta/sec)} = N A_n = \frac{64\pi^4 \nu_{nm}^3 N_n |R_{nm}|^2}{3h}$$

(9)

In more specific terms, the intensity of emission from a single vibration-rotation line may be written

$$I_{v'j', v''j''} = \frac{64\pi^4 \nu_{v'j'}^3 \nu_{v''j''} N_{v'j'} N_{v''j''}}{3h} \left| \sum_{i;k} R_{v''j''}^v R_{v'j'}^i \right|^2$$

(10)

where the matrix element is now summed over the individual transition matrix elements connecting the degenerate sublevels of each rotational state. The term $d_{v'j'}$ is equal to $2J' + 1$ which is the degeneracy of the emitting state. We now make the assumption that the transition matrix element is separable into three terms,

1) an element due to overlap of the rotational wave functions, also known as the rotational line strength, $S_{J''}^{J'}$,

2) a vibration-rotation interaction factor, $F_{v''j''}^{v'j'}$, and

3) the remaining vibrational contributions $|R_{v''j''}^v|^2$

A semiclassical approximation to the vibration-rotation interaction factor is

$$F = 1 - 4\gamma \theta_m$$

(11)
where \( \gamma = \omega_r / \omega_v \), the frequency ratio of rotational to vibrational motion, \( m = J' \) for an R branch and \( - (J'+1) \) for a P branch, and \( \theta = M_r / M_l \) which is derived from the dipole moment expansion about an equilibrium internuclear distance \( r_e \). In simple terms we may consider the intensity of a line to be proportional to the \( F \) factor so that

\[
I_{v'J'} (\text{energy/sec}) \propto (\omega_{v''J''}^{v'J'})^4 F_{v''J''}^{v'J'}
\]

(12)

where \( \omega \) is in cm\(^{-1}\). We may also write

\[
(\omega_{v''J''}^{v'J'})^4 = (\omega_o + 2Bm)^4 \approx \omega_o^4 \left( 1 + \frac{8B}{\omega_o} m \right) \]

(13)

where \( m \) is defined as above, \( \omega_o \) is the band origin and \( B \) is the rotational constant. If we now substitute Eqs. (11) and (13) into Eq. (12) we have

\[
I_{v'J'} = \omega_o^4 (1 + \frac{8B}{\omega_o} m)(1 - 4 \frac{\gamma}{\omega_v} \theta_m)
\]

(14)

We may replace the frequency ratio \( \gamma / \omega_v \) by \( 2B/\omega_o \) and now write

\[
I_{v'J'} = \omega_o^4 (1 + \frac{8B}{\omega_o} m)(1 - \frac{8B}{\omega_o} \theta_m)
\]

(15)

If \( \theta = 1 \) and we ignore the square term \((8Bm/\omega_o)^2\), Eq. (15) reduces to \( \omega_o^4 \). Thus in this case the effects of frequency variation and of the \( F \) factor are in opposition and to a good extent cancel each other. The approximation that \( \theta = 1 \) has been discussed by Polanyi\(^{31}\) and found to be satisfactory.\(^8\)
If we assume rotational equilibrium (to be further discussed later) the population of a particular rotational level is

\[ N_{v',J'} = \frac{N_v (2J'+1)}{Q_{rot}} \exp\left[-\frac{B_{v',J'}(J'+1)}{kT_r}\right] \]  \hspace{1cm} (16)

where \( Q_{rot} \) is the rotational partition function, \( B_{v'} \) is the rotational constant for vibrational level \( v' \) and \( T_r \) is the rotational temperature of the emitting species. We now combine Eqs. (10) and (16) along with the substitution that \( Q_{rot} = \frac{kT_r}{B_{v'}} \), and obtain as an expression for emission

\[ I_{v',J'}^{v'',J''} = \frac{64\pi^4 B_v^3 S_{J'}^J B_{v''}^S}{3\hbar kT_r} \frac{N_v}{N_{v'}} \exp\left[-\frac{B_{v',J'}(J'+1)}{kT_r}\right] |R_{v'}^v|^2 \]  \hspace{1cm} (17)

The rotational line strength factors have been calculated for HO assuming a model of coupling intermediate between Hund's cases a and b and are presented in Table III.32

2. Transition Probabilities

There have been several theoretical calculations of relative transition probabilities33–35 and one recent calculation from laboratory observation.36 From Eq. (8) we see that the transition probability behaves as

\[ A_{nm} \propto \frac{1}{nm} |R_{nm}|^2 \]

Using this relationship, the transition matrix elements calculated by Cashion35 can be combined with the most recently measured band origins29 to give a corrected set of transition probabilities. Those band origins
Table III. Hydroxyl Molecule Rotational Line Strengths, $S_{J'_{1/2}}^{J''}$

<table>
<thead>
<tr>
<th>$K$</th>
<th>$J$</th>
<th>$P$</th>
<th>$Q$</th>
<th>$R$</th>
<th>$J$</th>
<th>$p$</th>
<th>$q$</th>
<th>$r$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3/2</td>
<td>1.62</td>
<td>2.30</td>
<td></td>
<td>1/2</td>
<td>1.29</td>
<td>0.667</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>5/2</td>
<td>2.90</td>
<td>1.40</td>
<td>1.62</td>
<td>3/2</td>
<td>2.34</td>
<td>0.300</td>
<td>1.29</td>
</tr>
<tr>
<td>3</td>
<td>7/2</td>
<td>4.04</td>
<td>0.98</td>
<td>2.90</td>
<td>5/2</td>
<td>3.37</td>
<td>0.223</td>
<td>2.34</td>
</tr>
<tr>
<td>4</td>
<td>9/2</td>
<td>5.14</td>
<td>0.73</td>
<td>4.04</td>
<td>7/2</td>
<td>4.37</td>
<td>0.188</td>
<td>3.37</td>
</tr>
<tr>
<td>5</td>
<td>11/2</td>
<td>6.21</td>
<td>0.57</td>
<td>5.14</td>
<td>9/2</td>
<td>5.38</td>
<td>0.17</td>
<td>4.37</td>
</tr>
<tr>
<td>6</td>
<td>13/2</td>
<td>7.26</td>
<td>0.46</td>
<td>6.21</td>
<td>11/2</td>
<td>6.39</td>
<td>0.16</td>
<td>5.38</td>
</tr>
<tr>
<td>7</td>
<td>15/2</td>
<td>8.30</td>
<td>0.37</td>
<td>7.26</td>
<td>13/2</td>
<td>7.39</td>
<td>0.15</td>
<td>6.39</td>
</tr>
<tr>
<td>8</td>
<td>17/2</td>
<td>9.32</td>
<td>0.33</td>
<td>8.30</td>
<td>15/2</td>
<td>8.40</td>
<td>0.15</td>
<td>7.39</td>
</tr>
<tr>
<td>9</td>
<td>19/2</td>
<td>10.34</td>
<td>0.29</td>
<td>9.32</td>
<td>17/2</td>
<td>9.41</td>
<td>0.14</td>
<td>8.40</td>
</tr>
<tr>
<td>10</td>
<td>21/2</td>
<td>11.36</td>
<td>0.26</td>
<td>10.34</td>
<td>19/2</td>
<td>10.42</td>
<td>0.14</td>
<td>9.41</td>
</tr>
<tr>
<td>11</td>
<td>23/2</td>
<td>12.37</td>
<td>0.24</td>
<td>11.36</td>
<td>21/2</td>
<td>11.42</td>
<td>0.12</td>
<td>10.42</td>
</tr>
<tr>
<td>12</td>
<td>25/2</td>
<td>13.38</td>
<td>0.22</td>
<td>12.37</td>
<td>23/2</td>
<td>12.43</td>
<td>0.11</td>
<td>11.42</td>
</tr>
<tr>
<td>13</td>
<td>27/2</td>
<td>14.39</td>
<td>0.20</td>
<td>13.38</td>
<td>25/2</td>
<td>13.43</td>
<td>0.10</td>
<td>12.43</td>
</tr>
<tr>
<td>14</td>
<td>29/2</td>
<td>15.40</td>
<td>0.18</td>
<td>14.39</td>
<td>27/2</td>
<td>14.43</td>
<td>0.10</td>
<td>13.43</td>
</tr>
<tr>
<td>15</td>
<td>31/2</td>
<td>16.41</td>
<td>0.16</td>
<td>15.40</td>
<td>29/2</td>
<td>15.44</td>
<td>0.10</td>
<td>14.43</td>
</tr>
<tr>
<td>16</td>
<td>33/2</td>
<td>17.42</td>
<td>0.15</td>
<td>16.41</td>
<td>31/2</td>
<td>16.44</td>
<td>0.10</td>
<td>15.44</td>
</tr>
<tr>
<td>17</td>
<td>35/2</td>
<td>18.42</td>
<td>0.14</td>
<td>17.42</td>
<td>33/2</td>
<td>17.44</td>
<td>0.10</td>
<td>16.44</td>
</tr>
<tr>
<td>18</td>
<td>37/2</td>
<td>19.43</td>
<td>0.13</td>
<td>18.42</td>
<td>35/2</td>
<td>18.44</td>
<td>0.09</td>
<td>17.44</td>
</tr>
<tr>
<td>19</td>
<td>39/2</td>
<td>20.43</td>
<td>0.12</td>
<td>19.43</td>
<td>37/2</td>
<td>19.44</td>
<td>0.09</td>
<td>18.44</td>
</tr>
<tr>
<td>20</td>
<td>41/2</td>
<td>21.44</td>
<td>0.11</td>
<td>20.43</td>
<td>39/2</td>
<td>20.44</td>
<td>0.09</td>
<td>19.44</td>
</tr>
</tbody>
</table>
(in cm\(^{-1}\)) are listed in Table IV. Those bands underlined are the eleven bands observed in this work.

The probabilities calculated by Murphy\(^3\) from experimental observation vary significantly from other calculations in the ratio of the first overtone (\(\Delta v=2\)) transition probabilities to fundamental (\(\Delta v=1\)) transition probabilities. However when comparing only the bands observed in this work, all four available sets of probabilities agree moderately well. A comparison of the four sets of probabilities for the eleven observed bands, normalized to the 4-0 band, is presented in Table V a–d.

It was decided to use the values derived from Cashion's calculation for several reasons. His theoretical calculations are the most recent and as corrected to the best values of the band origins, should be most accurate. Murphy's calculations suffer from being based on experimental measurements. Carrington\(^3\) has concluded that it is extremely difficult to obtain good values of A\(_{nm}\) from observation of a steady state system because of the high degree of precision necessary in measuring vibrational populations.

Fortunately there is a corollary recognized by both Carrington and Polanyi\(^3\) that it is not necessary to have extremely accurate transition probabilities to calculate k\(_v\)'s or R\(_v\)'s (rate constants or rates for specific vibrational levels). For example, an error in a transition probability affects at the same time many terms which measure rates both into and out of a vibrational level. The rate constants we are looking for affect the balance of population in a
Table IV. Hydroxyl Radical Band Origins (cm$^{-1}$)

<table>
<thead>
<tr>
<th>v'\v''</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3750.57</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>6975.57</td>
<td>3404.93</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>10217</td>
<td>6646.02</td>
<td>3241.08</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>13295</td>
<td>9733.97</td>
<td>6319.63</td>
<td>3078.54</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>16211</td>
<td>12641</td>
<td>9235.57</td>
<td>5994.52</td>
<td>2916.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>18964</td>
<td>15393</td>
<td>11988</td>
<td>8746.8</td>
<td>5668.2</td>
<td>2752.25</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>21550</td>
<td>17980</td>
<td>14575</td>
<td>11334</td>
<td>8254.9</td>
<td>5339.0</td>
<td>2586.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>23966</td>
<td>20394</td>
<td>16990</td>
<td>13749</td>
<td>10670</td>
<td>7754.3</td>
<td>5002.0</td>
<td>2415.3</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>26203</td>
<td>22633</td>
<td>19227</td>
<td>15985</td>
<td>12909</td>
<td>9893.2</td>
<td>7239.6</td>
<td>4652.7</td>
<td>2237.4</td>
</tr>
</tbody>
</table>

-
Table V. Relative Transition Probabilities ($v'\rightarrow v''$)

<table>
<thead>
<tr>
<th>v' \ v''</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>1.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>1.28(1)</td>
<td>5.10</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>8.19(1)</td>
<td>15.46</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>1.52(1)</td>
<td>3.03</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>6.72(1)</td>
<td>8.50</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td></td>
<td>2.21</td>
<td>19.80</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

NOTE: $1.28(1) = 1.28 \times 10^{-1}$

<table>
<thead>
<tr>
<th>v' \ v''</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>1.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>1.79(1)</td>
<td>4.59</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>1.0</td>
<td>13.31</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>2.46(1)</td>
<td>3.46</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>9.31(1)</td>
<td>8.63</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td></td>
<td>2.73</td>
<td>20.63</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>v' \ v''</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>1.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>1.65(1)</td>
<td>4.69</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>9.48(1)</td>
<td>13.14</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>2.20(1)</td>
<td>3.17</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>8.63(1)</td>
<td>7.97</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td></td>
<td>2.50</td>
<td>16.80</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>v' \ v''</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>1.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>1.88(1)</td>
<td>4.55</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>9.87(1)</td>
<td>12.45</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>2.73(1)</td>
<td>3.08</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>9.32(1)</td>
<td>7.07</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td></td>
<td>2.36</td>
<td>14.11</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

-33-
level and are given by the net difference in the previously mentioned rates. To obtain relative rates of reaction into different vibrational levels, we are interested only in the relative value of those differences from one level to the next. The relative values would be little affected by changes in the absolute magnitude of a set of transition probabilities.

This is also demonstrated by noting that several researchers have calculated similar sets of $R_v$'s using different sets of transition probabilities. These results will be discussed in a later section.

3. Details of Calculation of Synthetic Spectrum

To actually calculate the synthetic spectrum it is necessary to assemble the known spectral quantities, the transition probabilities, and the equations governing the response of the instrument. These include the spectral slit function, the RC time constant, and the spectral response of the detector. Equation (17) is nearly complete for calculation, but it must be pointed out that the term $\nu_{v',J',v''J''}$ must be the exact frequency difference between levels $v',J'$ and $v'',J''$. This requires use of the rotational term values listed earlier (Eqs. 3a and 3b). For a line in the $^2\Pi_{3/2}$ multiplet we have

$$\nu_{v',J',v''J''} = \nu_o(v') - \nu_o(v'') + B_{v'} \left[ (J' + \frac{1}{2})^2 \Lambda^2 - \frac{1}{2} \sqrt{4(J'+\frac{1}{2})^2 + Y_{v'}(Y_{v'}-4)\Lambda^2} \right]$$

$$- D_{v',J'} - B_{v''} \left[ (J'' + \frac{1}{2})^2 \Lambda^2 - \frac{1}{2} \sqrt{4(J''+\frac{1}{2})^2 + Y_{v''}(Y_{v''}-4)\Lambda^2} \right] - D_{v''} J''^4$$

(18)
The same treatment follows for a line from the $^2\pi_{1/2}$ multiplet. For each multiplet there are three possibilities for a relationship between $J'$ and $J''$. They are

- **R branch**: $J' = \frac{5}{2}, \frac{7}{2}, \frac{9}{2}, \ldots$ \[ J'' = J' - 1 \]
  \[ J'' = \frac{41}{2} \]

- **Q branch**: $J' = \frac{3}{2}, \frac{5}{2}, \frac{7}{2}, \ldots$ \[ J'' = J' \]
  \[ J'' = \frac{41}{2} \]

- **P branch**: $J' = \frac{3}{2}, \frac{5}{2}, \frac{7}{2}, \ldots$ \[ J'' = J' + 1 \]

These substitutions are made for computational ease. Also shown are the limits of $J'$ for each branch. Equation (17) may now be rewritten as

\[ \frac{I_{v'}_{J'}}{I_{v''}_{J''}} = N_v \times [\text{all other factors}] \quad (19) \]

All the other factors are now known, so an entire spectrum at unit population may be calculated. Because the spectra in this experiment were obtained with wide slits, the intensity observed at some frequency $\nu_o$ is actually the sum of intensities of all lines falling within the spectral bandpass, convoluted against the spectral slit function. Because the spectral bandpass is a constant number of Angstroms, we will define the slit function in terms of wavelength. Calculated frequencies are converted to wavelengths using vacuum to air correction factors from Ref. 39.

\[ I(\lambda_o) = \sum_i I(\lambda_i) f[\lambda_i - \lambda_o] \quad (20) \]
Thus the intensity at observation wavelength, \( \lambda_o \), is the sum of intensities at \( i \) wavelengths (limits on \( i \) to be determined later) times a function of the difference between \( \lambda_i \) and \( \lambda_o \). As shown in Fig. 2, the spectral slit function has an approximate triangular form. We will define the function

\[
f(\lambda-\lambda_o) = 1 - \frac{|\lambda-\lambda_o|}{T} \quad |\lambda-\lambda_o| \leq T \quad (21a)
\]

\[
f(\lambda-\lambda_o) = 0 \quad |\lambda-\lambda_o| > T \quad (21b)
\]

where \( T \) is the spectral slit width (FWHM).

In an actual experiment, however, the amplifier applies an RC time constant to the signal which will have the effect of displacing the observed line center from the true line center. This effect will vary depending upon scan speed and the time constant. It is necessary to consider the response of a simple RC series circuit to an input voltage which behaves as Eqs. (21a-21b). This circuit will have a time constant \( T \) and we will define \( T \) to be the time necessary to scan over one spectral slit width.

\[
\text{scan speed} = \frac{T}{T}
\]

The reference time, \( t \), will be defined to be zero when \( \lambda_o = \lambda - T \) or

\[
t = \frac{\lambda_o - \lambda + T}{T}
\]

(22)
This equation holds for a scan in the direction of higher wavelength.

There are three time intervals in which the system response is of interest. First the input in each interval

1) $0 \leq t \leq T$ in which the input signal is

$$\frac{d f(\lambda - \lambda_0)}{dt} = \frac{t}{T}$$

2) $T \leq t \leq 2T$ in which the input signal is

$$f(\lambda - \lambda_0) \bigg|_{t=T} - (t-T) \frac{d f(\lambda - \lambda_0)}{dt} = 1 - \frac{t-T}{T}$$

3) $t > 2T$ in which the input signal is zero.

The response to the input signal in each of these time intervals is found by solving the differential equation governing the behavior of the RC circuit and setting the solutions equal at the boundaries. Doing this, we obtain

$$R_1 = \frac{T}{T} \left( \frac{t}{T} + e^{-t/T} - 1 \right) \quad 0 \leq t \leq T$$  \hspace{1cm} (23)

$$R_2 = \frac{T}{T} \left( 2 \frac{T}{t} - \frac{t}{T} + (1-2e^{T/T})e^{-t/T} + 1 \right) \quad T \leq t \leq 2T$$  \hspace{1cm} (24)

$$R_3 = \frac{T}{T} (1-e^{-T/T})^2 e^{-t/T} \quad t > 2T$$  \hspace{1cm} (25)

If we substitute for $t$ according to Eq. (22), we obtain the corresponding set of equations in terms of wavelength.
Under the conditions in which most spectra were obtained; $\tau = 0.1 \text{ sec}$, $\tau = 26.2\text{Á}$, and $\tau = 3.1 \text{ sec}$, the spectral slit function has decayed to zero well within the arbitrary limits of $\lambda_o \pm 2\tau$. However, since only 118 rotational line strength values are known, it was simplest to just sum over all of them. This defines the limits of summation in Eq. (20).

This now constitutes all the information necessary to calculate a synthetic hydroxyl radical spectrum with unit population in each vibrational state. A description and listing of the program written for this purpose is found in Appendix I-A.

4. Population Fitting and Rotational Temperatures

Because the set of bands observed in this work overlaps considerably, the emission intensity observed at some wavelength is the sum of contributions of all bands which have a line at that wavelength. The specific contribution of a band is a product of the relative population of the emitting state times the calculated transition probability factor. This is shown in Eq. (26).
The program described in the previous section actually calculates the unit population contribution of each of the eleven bands observed in this work and stores them for later use.

The method of determining relative populations of the six emitting vibrational states observed in this work (v=9,8,7,6,5,4) is to fit the synthetic spectrum point by point to an observed spectrum with an assumed set of relative populations. Because the problem is highly overdetermined; i.e. 3000 or more spectral points to determine six populations, a least squares fitting program is used to vary the set of populations until the smallest $F$ is found where $F$ is the sum of the squares of the residuals.

$$F = \sum_{\lambda} (I_\lambda(i) - I_\lambda(n))^2$$

where $i$ is the index for the observed spectrum and $n$ is the index for the calculated spectrum. Examples of the unit synthetic spectrum, an observed spectrum, and the result of fitting are shown in Figs. 6, 7, and 8. A description and listing of the fitting program is found in Appendix I-B.

The shape of an individual band at low resolution and the intensity of the rotational lines within that band depend upon the rotational temperatures as shown in Eq. (17). Rotational temperature in this work was determined by calculating synthetic spectra at several
Fig. 6. Unit synthetic spectrum.
Fig. 7. An observed spectrum.
Fig. 8. Fitted spectrum . . . observed spectrum  
XBL 745-6299  
--- calculated spectrum
different temperatures and finding which one gives the best fit to the observed spectrum. This is admittedly only a very rough determination because it assumes the same $T_R$ for each vibrational state, but there was no need to determine a better value of $T_R$. Figures 6, 9, and 10 demonstrate the change in the shape and intensity of lines at three different rotational temperatures; 1500°K, 600°K, and 2500°K, respectively.

The method of analysis just described finds a set of relative populations from a 3000 point spectrum observed at some specific pressure. To obtain many sets of populations at different pressures for the purpose of determining kinetic data required many spectra. It was quickly realized that this procedure overdetermines spectral data and severely limits the amount of pressure dependence data. An alternative and much more viable procedure is to scan the pressure range at fixed wavelength. This may be done at several peaks selected from the hydroxyl spectrum. A pressure scan of ten different peaks yields sufficient spectral data to determine a set of six relative vibrational populations by the least squares method and at the same time yields much better pressure data. A typical intensity vs. pressure plot is shown in Fig. 11. The points are the data and the solid line is the best 7th order polynomial fit to the data. The program to calculate this fit is described in Appendix I-C. The fit is done merely for the purpose of determining intensity at convenient pressure intervals rather than relying on the raw data which is determined at random pressures. Table VI lists the peaks observed in this type of
Fig. 9. Unit synthetic spectrum.
Fig. 10. Unit synthetic spectrum. 

$T_R = 2500^\circ K$
Fig. 11. Decay of intensity at 7250Å.
experiment and the bands which contribute to each peak. Table VII lists the peaks and the relative contribution of each band at unit population. The peaks for which the wavelength, \( \lambda \), is underlined are those most commonly used.

C. Determination of Kinetic Rate Constants

With a full set of vibrational populations versus reactant pressure, it is now necessary to conceive some model to relate populations to pressure. The technique of chemiluminescence has the advantage of being able to follow the exact quantum level and energy distribution of a multi-level system of intermediates or products in a chemical reaction. However in trying to extract kinetic data from chemiluminescence observation, the presence of a complex multi-level system is a distinct disadvantage. The flux of molecules through any particular level is due to many factors; radiation, quenching, reaction, chemical activation, etc., so the particular kinetic process one is trying to follow is only one of many competing processes.

The observer of multi-state vibrational chemiluminescence is in the obscure world between the two state easily resolved experiment and the classical totally non-resolved kinetics experiment. His task is much more difficult and his answers more uncertain than those of the two state experimenter, but neither can he ignore the resolved data at hand and present non resolved rate constants to explain his observations. With this in mind we set about developing a model to explain the observed behavior of the hydroxyl system.
Table VI. Hydroxyl Spectrum Peaks and their Band Composition

<table>
<thead>
<tr>
<th>( \lambda (\text{Å}) )</th>
<th>Bands</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5553</td>
</tr>
<tr>
<td>2</td>
<td>5879</td>
</tr>
<tr>
<td>3</td>
<td>6071</td>
</tr>
<tr>
<td>4</td>
<td>6147</td>
</tr>
<tr>
<td>5</td>
<td>6189</td>
</tr>
<tr>
<td>6</td>
<td>6252</td>
</tr>
<tr>
<td>7</td>
<td>6470</td>
</tr>
<tr>
<td>8</td>
<td>6709</td>
</tr>
<tr>
<td>9</td>
<td>6837</td>
</tr>
<tr>
<td>10</td>
<td>7087</td>
</tr>
<tr>
<td>11</td>
<td>7250</td>
</tr>
<tr>
<td>12</td>
<td>7478</td>
</tr>
<tr>
<td>13</td>
<td>7528</td>
</tr>
<tr>
<td>14</td>
<td>7577</td>
</tr>
<tr>
<td>15</td>
<td>7632</td>
</tr>
<tr>
<td>16</td>
<td>7723</td>
</tr>
<tr>
<td>17</td>
<td>7858</td>
</tr>
<tr>
<td>18</td>
<td>8147</td>
</tr>
<tr>
<td>19</td>
<td>8289</td>
</tr>
</tbody>
</table>
Table VII. Hydroxyl Peaks and Relative Band Contribution ($T_R = 1500^\circ K$)

<table>
<thead>
<tr>
<th>$\lambda$(Å)</th>
<th>9</th>
<th>8</th>
<th>7</th>
<th>6</th>
<th>5</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5553</td>
<td></td>
<td>1.98(2)</td>
<td>2.07(4)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>5879</td>
<td>7.83(2)</td>
<td>2.60(3)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>6071</td>
<td>2.31(2)</td>
<td>3.74(4)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>6147</td>
<td>1.72(2)</td>
<td>4.99(4)</td>
<td>1.97(2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>6189</td>
<td>1.41(2)</td>
<td>6.36(5)</td>
<td>6.75(3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>6252</td>
<td>2.18(1)</td>
<td>6.31(3)</td>
<td></td>
<td></td>
<td>5.28(3)</td>
</tr>
<tr>
<td>7</td>
<td>6470</td>
<td>4.83(2)</td>
<td>3.58(3)</td>
<td>1.14(1)</td>
<td>1.29(3)</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>6709</td>
<td>3.17(2)</td>
<td>3.21(4)</td>
<td></td>
<td>2.54(2)</td>
<td>2.84(4)</td>
</tr>
<tr>
<td>9</td>
<td>6837</td>
<td>1.46(2)</td>
<td>3.96(1)</td>
<td>1.58(2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>7087</td>
<td>5.75(3)</td>
<td></td>
<td>8.94(2)</td>
<td>1.22(3)</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>7250</td>
<td>9.73(1)</td>
<td>2.68(2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>7478</td>
<td>4.31(4)</td>
<td>2.88(1)</td>
<td>1.34(2)</td>
<td></td>
<td>1.59(1)</td>
</tr>
<tr>
<td>13</td>
<td>7528</td>
<td>2.69(1)</td>
<td></td>
<td>4.01(2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>7577</td>
<td>2.39(1)</td>
<td>7.27(3)</td>
<td></td>
<td>2.16(2)</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>7632</td>
<td>2.03(1)</td>
<td>5.82(3)</td>
<td></td>
<td>2.74(2)</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>7723</td>
<td>1.90(0)</td>
<td>2.17(3)</td>
<td>5.22(3)</td>
<td></td>
<td>1.61(3)</td>
</tr>
<tr>
<td>17</td>
<td>7858</td>
<td>6.15(1)</td>
<td>1.22(3)</td>
<td>8.10(1)</td>
<td>5.31(3)</td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>8147</td>
<td>4.55(1)</td>
<td>2.81(2)</td>
<td></td>
<td>1.56(1)</td>
<td>6.16(3)</td>
</tr>
<tr>
<td>19</td>
<td>8289</td>
<td>3.29(1)</td>
<td></td>
<td>2.33(0)</td>
<td>3.66(2)</td>
<td>2.93(3)</td>
</tr>
</tbody>
</table>

**NOTE:** $1.98(2) = 1.98 \times 10^{-2}$
1. **Mechanism of the Hydroxyl Radical System**

If we look at a general vibrational state \( v \), there are a number of processes that may populate or depopulate this state.

**Formation Processes**
- Reaction of \( H + O_3 \)
- Reaction of primary \( H \)
- Reaction of secondary \( H \)
- Collisional cascading from levels above
- Collisional excitation from levels below (consider only \( v-1 \rightarrow v \))
- Radiative transitions from levels above

**Destruction Processes**
- Radiative transitions to levels below
- Collisional cascading to levels below
- Collisional excitation to levels above (consider only \( v \rightarrow v+1 \))
- Deactivation at the wall
- Pumping out of the system
- Reaction
  - With \( O_3 \) or other added species
  - With \( HO \)

Very quickly some of the processes may be shown to be negligible. A simple measure of the pumping speed showed \( k_p \approx 0.2 \text{ sec}^{-1} \) so this term may be neglected. Collisional excitation may also be neglected because the Boltzmann factor for excitation, \( e^{-\Delta E/RT} \), is approximately \( 4 \times 10^{-6} \) assuming average vibrational spacing of \( \approx 7.5 \text{ kcal} \). We will also make two assumptions. One is that loss of vibrational energy
by collisional quenching is restricted to one quantum at a time.

Single quantum transitions are expected to be the dominant process for several reasons. The $\Delta \nu = 4,5$ and 6 radiative transitions observed in this work have first order rate constants on the order of $1.0 \times 10^{-2}$ sec$^{-1}$ while $\Delta \nu = 1$ transitions for hydroxyl have first order rate constants of approximately 10 sec$^{-1}$. Collisional transitions are expected to behave similarly to radiative transitions, so multiquantum processes would be very slow compared to single quantum processes. Also, as will be noted in later discussion, current energy transfer theories predict at most a ten percent contribution of $\Delta \nu = 2$ transitions to an overall quenching rate. This single quantum restriction forces each hydroxyl to cascade through all lower vibrational state and thereby makes the rate at which one state is quenched equal to the rate at which the next lower state is populated by collisional cascade. The other assumption is that quenching at the wall is total so that it is governed solely by how rapidly molecules migrate to the walls. The coefficient of gaseous diffusion ($D$) is proportional to $1/[M]$, but the root mean square displacement of a gas is proportional to $\sqrt{D}$, so the rate of quenching at the wall will be proportional to $1/[M]^{1/2}$.

The remaining processes may be described by the following reaction scheme.

\[
\begin{align*}
H + O_3 & \rightarrow HO(v \leq 9) + O_2 & k_1 \\
HO(v) & \rightarrow HO(v') + h\nu (v' < v) & \tau_{v,v'}^{-1} \\
HO(v) + M & \rightarrow HO(v-1) + M & k_q^v \\
HO(v) + O_3 & \rightarrow products & k_2^v \\
HO(v) + HO(v') & \rightarrow products (v'=0,1 \ldots 9) & k_{3}^{v,v'} \\
wall deactivation & & k_w
\end{align*}
\]
A steady state analysis of the system; i.e. setting $\frac{d[HO]}{dt} = 0$,
and solving for a general vibrational state gives

$$[HO]_v = \frac{f_v k_1 [H][O_3] + \sum_{v'=v+1}^{9} \tau_{v,v'}^{-1} [HO]_{v'} + k_{q}^{v+1,v} [HO]_{v+1}[M]}{\tau_v^{-1} + k_2 [O_3] + k_q^v [M] + \sum_{v'=0}^{9} k_3^{v'} [HO]_{v'} + k_\omega / [M]^{1/2}}$$

(27)

where $f_v$ is the fraction of hydroxyls produced by the reaction of $H + O_3$ which populates state $v$. The other symbols all have standard meanings.

The point of this investigation was to determine $k_1$ with various $q$ M gases and $k_2$ with ozone. The concentrations which could be measured were $[O_3]$, $[M]$, and relative $[HO]_v$. The rate constant $k_1$ has been measured to be $2.6 \times 10^{-11}$ cm$^3$/molecule-sec. The radiative lifetime of state $v=9$ was measured by Worley and co-workers and this value $(6.4 \pm 1.4) \times 10^{-2}$ seconds was used to calculate the inverse lifetime for each transition of interest in this work.

The population fraction, $f_v$, may be found by measuring emission intensity vs. pressure to as low a pressure as possible and then extrapolating to zero pressure. The wall quenching term in Eq. (27) does not become infinite because migration to the walls is limited by molecular speed, but wall quenching does become the dominant loss process at zero pressure. Equation (27) is reduced to $f_v k_1 [H][O_3]$ (quenching rate). Thus the population at zero pressure is directly proportional to $f_v$. These results will be discussed in section IV-A.
The wall quenching constant, because it is actually a measure of how rapidly a hydroxyl molecule leaves the field of view on its way to the wall, is assumed to be identical for all vibrational levels. Because vibrational state \( v=9 \) is populated only by chemical reaction, any increased intensity at low pressure as \( M \) is increased must be attributed to a decrease in the rate at which molecules leave the field of view. If the \( M \) gas used is an inefficient quencher, Eq. (27) may be written in terms of the intensity of the 9–4 transition.

\[
\frac{1}{I_{9-4}} = \frac{\tau_{9}^{-1} + k_{2}^{9}[O_{3}] + k_{w}^{9}/[M]^{1/2}}{\tau_{9,4}^{-1} k_{1} f_{9}[H][O_{3}]}\]

A plot of \( 1/I \) versus \( 1/[M]^{1/2} \) should yield a straight line for which the slope divided by the intercept is \( k_{w}/(\tau_{9}^{-1} + k_{2}^{9}[O_{3}]) \). The experiments and results will be described in section IV-B.

It is important to notice that the numerator of Eq. (27) is written in terms of relative hydroxyl population and the denominator in terms of absolute concentration. This requires the remaining unknown concentration, \([H]\), to be determined relative to hydroxyl concentrations. Because \([H]\) could not be measured in this system it becomes the first fitting parameter in the computation to be described in the next section. In the denominator of Eq. (27) is the difficult term involving hydroxyl–hydroxyl reactions;

\[ \sum_{v'=0}^{9} k_{3}^{v'v} [H0]_{v'} \]

The concentrations are needed in absolute terms, but are not available and the rate constants for vibrationally excited hydroxyl reacting with other vibrationally excited hydroxyl are not known. It may be expected that the term for hydroxyl reacting with itself is small, but at low pressures hydroxyl concentrations becomes a much larger
fraction of the total species present so it is not wise to ignore the
term, especially when the rate constants are not known. This problem
is dealt with fairly easily. The rate constant $k_{3}^{0,0}$ has been measured\textsuperscript{42} to be $1.4 \times 10^{-12} \text{cm}^{3}/\text{molec-sec}$ and it has been suggested\textsuperscript{43} that the rate constant be $3 \times 10^{-11} \text{cm}^{3}/\text{molec-sec}$ for all $v>0$. However it is felt that
the rate constant is probably $v$ dependent so the following values were used.

<table>
<thead>
<tr>
<th>$v$</th>
<th>9</th>
<th>8</th>
<th>7</th>
<th>6</th>
<th>5</th>
<th>4</th>
<th>3</th>
<th>2</th>
<th>1</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_{3}^{v}$</td>
<td>2.3</td>
<td>1.8</td>
<td>1.4</td>
<td>1.1</td>
<td>8.9</td>
<td>6.9</td>
<td>5.4</td>
<td>4.2</td>
<td>3.2</td>
<td>2.5</td>
</tr>
</tbody>
</table>

(-11) (-11) (-11) (-11) (-12) (-12) (-12) (-12) (-12)

In the computation the sum is obtained by multiplying the relative
population of each state with the appropriate rate constant and then
multiplied by a parameter, $FCONC$, which is the proportionality constant
between relative and absolute populations. Then with the doubtless
large inaccuracies, it is hoped that the fitting procedure calculates
a small enough $FCONC$ that the term is insignificant under most conditions.
Fortunately this proved to be the case.

2. Computational Model of the Hydroxyl Radical System

After having defined a steady state model of the hydroxyl system
and having dealt with some of the unknowns in the model, we may set
up the actual computational form and procedures. Equation (27) may
be rewritten

$$[\text{HO}]_{v} = \frac{x(1)k_{1}[O_{3}] + \sum_{v'=v+1}^{9} \tau_{v'}^{-1}[\text{HO}]_{v'} + x(2)[\text{HO}]_{v+1}[M]}{\tau_{v}^{-1} + k_{2}^{v}[O_{3}] + x(4) \sum_{v'=0}^{9} k_{3}^{v'}[\text{HO}]_{v'} + x(5)/[M]^{1/2}}$$

Equation (28)
where $x(1) = f_v[H]$, $x(2) = k_{q_v}^{v+1,v}$, $x(3) = k_q^v$, $x(4) = \text{FCONC}$, and $x(5) = k_w$. The set of parameters $x(1)-x(5)$ are set up so the computer program has the capability of finding best values for all of them, but in actual practice no more than two or three parameters are allowed to vary in any computation. A value for $x(5)$ was determined by an independent experiment so it was held constant. After a few experiments, a most likely value for $x(4)$ was determined so it too could be held constant.

An additional feature of this system is that vibrational level $v=9$ is the highest level populated and is populated only by chemical reaction. Thus there is no rate constant $k_{q_v}^{v+1,v}$ when determining the rate constant $k_q^9$. The rate constant $k_q^9$ then becomes $k_q^{9,8}$ when determining $k_q^8$, etc., because the model restricts transitions to one level at a time. This finally reduces the number of parameters to two which are easily determined when Eq. (28) is fit to 15-20 sets of population vs. pressure data.

Equation (28) is set up for determination of quenching constants and requires prior knowledge of the rate constants for reaction of HO(v) + $O_3$. To determine these rate constants, Eq. (28) must be modified slightly. In experiments for this purpose, concentrations of species other than ozone were kept extremely low, so the terms involving quenching drop out of the equation. The rate constant of interest, $k_q^v$, becomes the parameter $x(3)$. However one further complication is that $[H]$ does not remain constant with pressure when the pressure increase is due to increased ozone. There are two varieties of hydrogen atoms in the system; primary or those produced by the microwave discharge, and secondary, or those produced by the reaction of HO(v) with $O_3$. 
The exact partitioning of products is unknown. Because the behavior of $[H]$ with pressure is unknown, but it is known that $[H]$ is dependent upon $[O_3]$ and $[HO_v]$, we need a model that allows $[H]$ to vary as a function of $[O_3]$ and $[HO_v]$ with some parameter to account for unknown proportionality factors. Consider the following:

flow in $\rightarrow$ H (constant input from microwave discharge)

$HO(v) + O_3 \rightarrow H + 2O_2 \quad k_4^v$

$H + O_3 \rightarrow HO(v \leq 9) + O_2 \quad k_1$

These are the most important reactions involving production or destruction of H atoms. From this model we may write

$$\frac{d[H]}{dt} = -k_1[H][O_3] + [O_3] \sum_{v=0}^{9} k_4^v [HO_v] + \text{(flow in)} = 0$$

$$[H] = \frac{(\text{flow in}) + [O_3] \sum_{v=0}^{9} k_4^v [HO_v]}{k_1[O_3]}$$

Because $k_4^v$ is not known and $[HO_v]$ is known only for $v=4-9$, it is necessary to rewrite this as

$$[H] = \frac{(\text{flow in}) + [O_3]k_4 \sum_{v=4}^{9} [HO_v]}{k_1[O_3]}$$

If this is substituted into the first term in the numerator of Eq. (27) and written in terms of parameters, that first term becomes,
where \( x(1) \) accounts for a constant input of H atoms and \( x(2) \) is some "average" rate constant for the production of secondary hydrogen. The final equation for determining \( \text{HO}(v) + \text{O}_3 \) rate constants becomes

\[
[\text{HO}]_v = \frac{x(1) + x(2) [\text{O}_3] \sum_{v=4}^{9} [\text{HO}]_v + \sum_{v'=v+1}^{9} \frac{1}{\tau_v} [\text{HO}]_{v'}}{\tau_v^{-1} + x(3) [\text{O}_3] + x(4) \sum_{v'=0}^{9} k_{3}^{v'v} [\text{HO}]_{v'} + x(5)/[M]^{1/2}}
\] (29)

With \( x(4) \) and \( x(5) \) held constant, three parameters remain to be evaluated.

Equations (28) and (29) are the final mathematical models used to describe the hydroxyl system and to evaluate the rate constants \( k_q^v \) or \( k_2^v \). Given a set of \( [\text{HO}]_v \), \( [\text{O}_3] \), and \( [M] \) data and an initial set of parameters, the right hand side (RHS) of the equation predicts a value of \( [\text{HO}]_v \). Typically 15-20 sets of data are used so the system is overdetermined. The parameters are then varied until a specified function is minimized. The function in this case is

\[
F = \sum_n ([\text{HO}]_v^{\text{observed}} - [\text{HO}]_v^{\text{calculated}})^2
\]

The minimization of the function is carried out by a simplex procedure.

A description and listing of the computer program will be found in Appendix I-D.

A choice of minimization method depends on how much is known about the function \( F \). The possibilities are

a) only \( F \) is well defined
b) the first derivatives of \( F \) exist
c) the second derivatives exist and are reasonably continuous
d) the second derivative matrix is positive definite
The variable metric minimization method, if used to determine vibrational populations, is very fast in the vicinity of the minimum if \( F \) is well behaved (i.e. the area around the minimum is quadratic), but is very slow if \( F \) is badly behaved or if the initial guess is far from the minimum. The method also tends to find local minima if the function is first sampled far from the true minimum. For these reasons an alternate method, the simplex minimization procedure of Nelder and Mead\(^{44} \) was chosen.

In this method, the information known about the function \( F(x_1, \ldots x_n) \) is contained in \( n+1 \) points which form a simplex. A simplex is the simplest \( n \)-dimensional geometrical figure with \( n+1 \) corners: a triangle for \( n=2 \), a tetrahedron for \( n=3 \), etc. From the starting point a local minima is found along each coordinate axis by coordinate variation. These minima plus the starting point define the initial simplex. In each iteration, the function is evaluated at a point \( P^* \) found by reflecting the worst point \( P_H \) of the simplex into the center of gravity \( \bar{P} \) of the remaining points.

\[
\begin{array}{c|c|c|c|c}
& P_H & P** & P & P* & P** \\
\hline
\end{array}
\]

If \( F(P^*) \) is good relative to the known simplex points, \( P_H \) is replaced by \( P^* \). Otherwise another point, \( P^{**} \), is evaluated somewhere along the \( P_H, \bar{P} \) line. Now depending upon how good \( F(P^*) \) and \( F(P^{**}) \) are compared to the known simplex points, one of several options for the replacement of \( P_H \) or for evaluating an entirely new simplex is chosen. Iteration continues until convergence. Convergence is defined as
\[ F(P_H) - F(P_L) < \text{EPSI} \]

where \( P_H \) is the worst point of the simplex and \( P_L \) the best. EPSI is a user defined tolerance on the minimum function value.
IV. RESULTS AND DISCUSSION

A. Initial Vibrational Population Distributions and Vibrational Temperature

The leading term in Eq. (27) is $f_v$, which is the fraction of excited hydroxyls produced in vibrational state $v$ by the initial chemical reaction. This term could be left to the whims of the fitting program because it is always linked with the unknown [H], but it has significant importance in its own right as a measure of energy distribution in products of a chemical reaction.

As described in section III.C.1, $f_v$ was determined by setting up a very low pressure emission in the range of $3 \times 10^{-4}$ Torr and then adding an M gas to a total pressure of about $15 \times 10^{-4}$ Torr. Vibrational populations were then extrapolated back to zero pressure and the intercept at zero pressure was assumed to be directly proportional to $f_v$. Figures 12 and 13 show two typical plots of vibrational population behavior with M being Ar and $O_2$, respectively. A summary of the findings, normalized to $f_g=1.0$ are presented in Table VIII. In cases where the intercept was negative, $f_v$ was set equal to zero. A negative intercept, though sounding unusual, is an unexplained but common artifact of determining initial population distributions. Both Harrison$^4$ in his observation of the airglow and Smith$^{45}$ in observing CO chemiluminescence compute negative rates of activation for some vibrational levels. This artifact remains unexplained due to the complexity of a multi-level system. Because of the uncertainties in these numbers, they were used only as a guideline in rate constant calculations and were applied strictly only if the calculation converged to an unrealistic minimum.
Fig. 12. Vibrational populations extrapolated to zero pressure.
Fig. 13. Vibrational populations extrapolated to zero pressure.
Table VIII. Relative Initial Vibrational Population Distributions

<table>
<thead>
<tr>
<th>M _gas</th>
<th>M _9</th>
<th>M _8</th>
<th>M _7</th>
<th>M _6</th>
<th>M _5</th>
<th>M _4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>1.0</td>
<td>.81</td>
<td>.43</td>
<td>0</td>
<td>.23</td>
<td>0</td>
</tr>
<tr>
<td>Ar</td>
<td>1.0</td>
<td>.52</td>
<td>.02</td>
<td>.10</td>
<td>.40</td>
<td>.27</td>
</tr>
<tr>
<td>H\textsubscript{2}</td>
<td>1.0</td>
<td>.83</td>
<td>.57</td>
<td>.51</td>
<td>.26</td>
<td>.15</td>
</tr>
<tr>
<td>N\textsubscript{2}</td>
<td>1.0</td>
<td>.52</td>
<td>.60</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>O\textsubscript{2}</td>
<td>1.0</td>
<td>1.01</td>
<td>.08</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>D\textsubscript{2}</td>
<td>1.0</td>
<td>.68</td>
<td>.49</td>
<td>.43</td>
<td>.20</td>
<td>0</td>
</tr>
<tr>
<td>Avg.</td>
<td>1.0</td>
<td>.73</td>
<td>.37</td>
<td>.17</td>
<td>.18</td>
<td>.07</td>
</tr>
</tbody>
</table>
These numbers agree quite well with those found recently by other investigators using a wide variety of experimental techniques. A comparison is shown in Table IX. There is significant agreement that most, if not all, of the initial distribution falls into vibrational levels \( v=8 \) and 9.

Another quantity of interest when discussing energy distribution in reaction products is the vibrational temperature. It is not reasonable to expect the initial "collision-free" distribution to fit a Boltzmann distribution, but in practice each investigator has some "working" distribution which is expected to be dependent on the pressure and quite possibly to be characterized by some Boltzmann temperature.

The vibrational temperature relating any two relative vibrational populations is given by the well known formula

\[
\frac{N_i}{N_j} = \frac{e^{-\epsilon_i/kT}}{e^{-\epsilon_j/kT}}
\]

Solving for \( T_{\text{vib}} \) yields

\[
T_{\text{vib}} = \frac{-[(\epsilon_i - \epsilon_j)/k]}{\ln\left(\frac{N_i}{N_j}\right)}
\]

Some typical populations and the pressures at which they were observed are listed in Table X. Anytime \( N_{v+1} > N_v \) for any \( v \), the distribution is non-Boltzmann. This occurs in all four distributions where \( N_8 > N_7 \). For the three distributions at lower pressure the \( N_9/N_8 \) ratio yields
Table IX. Comparison of Recent Determinations of \( f_v \).

<table>
<thead>
<tr>
<th>( f_9 )</th>
<th>( f_8 )</th>
<th>( f_7 )</th>
<th>( f_6 )</th>
<th>( f_5 )</th>
<th>( f_4 )</th>
<th>( f_3 )</th>
<th>( f_2 )</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>.87</td>
<td>.50</td>
<td>.40</td>
<td>.35</td>
<td>.32</td>
<td>.26</td>
<td></td>
<td>8</td>
</tr>
<tr>
<td>1.0</td>
<td>.25</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>7</td>
</tr>
<tr>
<td>1.0</td>
<td>1.14</td>
<td>.17</td>
<td>0</td>
<td>.10</td>
<td>.21</td>
<td>-0.8</td>
<td></td>
<td>4</td>
</tr>
<tr>
<td>1.0</td>
<td>.73</td>
<td>.37</td>
<td>.17</td>
<td>.18</td>
<td>.07</td>
<td></td>
<td></td>
<td>This work</td>
</tr>
</tbody>
</table>
Table X. Typical Vibrational Population Distributions (normalized to \( N_4 = 1.0 \)).

<table>
<thead>
<tr>
<th>M gas</th>
<th>Pressure (Torr)</th>
<th>( N_4 )</th>
<th>( N_5 )</th>
<th>( N_6 )</th>
<th>( N_7 )</th>
<th>( N_8 )</th>
<th>( N_9 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>( 6 \times 10^{-4} )</td>
<td>1.0</td>
<td>.40</td>
<td>.19</td>
<td>.18</td>
<td>.24</td>
<td>.20</td>
</tr>
<tr>
<td>D(_2)</td>
<td>( 10 \times 10^{-4} )</td>
<td>1.0</td>
<td>.60</td>
<td>.30</td>
<td>.25</td>
<td>.32</td>
<td>.28</td>
</tr>
<tr>
<td>N(_2)</td>
<td>( 11 \times 10^{-4} )</td>
<td>1.0</td>
<td>.14</td>
<td>.07</td>
<td>.05</td>
<td>.06</td>
<td>.06</td>
</tr>
<tr>
<td>Ar</td>
<td>( 60 \times 10^{-4} )</td>
<td>1.0</td>
<td>.14</td>
<td>.10</td>
<td>.14</td>
<td>.26</td>
<td>.17</td>
</tr>
<tr>
<td>H(_2)</td>
<td>( 59 \times 10^{-4} )</td>
<td>1.0</td>
<td>.78</td>
<td>.28</td>
<td>.19</td>
<td>.23</td>
<td>.22</td>
</tr>
</tbody>
</table>
a temperature of $\sim 20,000^\circ$K whereas the $N_6/N_5$ ratio yields a temperature of $\sim 5600^\circ$K. The higher pressure distribution with $H_2$ very roughly fits a Boltzmann distribution of $10,000^\circ$K. Naturally this and all other estimates of a vibrational temperature pretend only to fit up to $v=9$ because higher levels are not populated at all. Since it is expected that at least $10^3$ collisions are needed to thermalize a vibrational distribution, the results at these low pressures are not at all unusual.

For comparison, Garvin and co-workers, working at a total pressure of 2-5 Torr, found a vibrational temperature of $\sim 9250^\circ$K. Harrison calculated $T_{\text{vib}} = 10800^\circ$K from an observation of the airglow. Murphy was unable to fit a Boltzmann temperature to his populations observed at 4-8 Torr. However Polanyi reports a much lower temperature of $\sim 5000^\circ$K at a total pressure of $7 \times 10^{-3}$ Torr. This was due to significant quenching at the wall attested to by his report of a rotational temperature exactly equal to the wall temperature ($100^\circ$K).

B. Determination of the Wall Quenching Constant

Another term in Eq. (27) which can be independently solved for is the wall quenching constant, $k_w$. As described in section III.C.1, $k_w$ is inversely proportional to $[M]^{1/2}$. Repeating Eq. (28)

$$\frac{1}{I_{9-4}} = \frac{\tau_{9}^{-9} + k_2^9[O_3] + k_w/[M]^{1/2}}{\tau_{9,4}^{-9} k_f [H][O_3]}$$

(28)
we see that plotting $1/I$ vs. $1/[M]^{1/2}$ yields a straight line for which the slope/intercept is $k_w/(\tau_9^{-1} + k_2^9[O_3])$. Plots for three experiments are shown in Fig. 14. The curvature exhibited is expected due to the complex dependence of emission intensity on pressure at higher pressure. (See Eq. 27). At low pressure the linear dependence on $1/[M]^{1/2}$ is quite clear. The data and results are shown in Table XI. The value of $k_2^9$ used was an early value determined before $k_w$ was fixed. Except at very low pressures the wall quenching term is insignificant, and no attempt was ever made to find rate constants at such low pressures, so $k_w$ was not revised when a final value of $k_2^9$ was found. The change in $k_w$ due to a change in $k_2^9$ was smaller than the uncertainty, so a revision of $k_w$ would have no meaning.

C. Rotational Temperature

Another quantity of interest when studying excited products of a chemical reaction is the temperature which characterizes the rotational distribution. As described in section III B.4, a rough rotational temperature for this work was determined by fitting several synthetic spectra to an observed spectrum. In an attempt to better define this quantity, a few higher resolution spectra were recorded with a spectral slit width (FWHM) of 13.1 Å. Figures 15a, b and 16a,b show two such spectra fitted to synthetic spectra calculated at 1500ºK and 3000ºK. The spectrum in Fig. 15 was recorded at $1.1\times10^{-3}$ Torr and that in Fig. 16 at $12\times10^{-3}$ Torr. It is evident that 1500ºK is too low at both pressures, though fairly close at the higher pressure. A temperature
Fig. 14. Determination of wall quenching constant.
Table XI. Derivation of Wall Quenching Constant

\[ k_w^9 = 9.5 \times 10^{-12} \text{ cm}^3/\text{molecule-sec} \quad \tau_9^{-1} = 15.6 \text{ sec}^{-1} \]

<table>
<thead>
<tr>
<th>Exp.</th>
<th>([O_3]) (molecule/cm(^3))</th>
<th>Slope</th>
<th>Intercept</th>
<th>Slope/intercept</th>
<th>(k_w)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>(1.2 \times 10^{12})</td>
<td>67.5</td>
<td>(2.9 \times 10^{-5})</td>
<td>7.42 \times 10^6</td>
<td>(2.0 \times 10^8)</td>
</tr>
<tr>
<td>II</td>
<td>(1.8 \times 10^{12})</td>
<td>37.3</td>
<td>(6.2 \times 10^{-5})</td>
<td>6.02 \times 10^6</td>
<td>(2.0 \times 10^8)</td>
</tr>
<tr>
<td>III</td>
<td>(1.6 \times 10^{12})</td>
<td>27.7</td>
<td>(7.0 \times 10^{-5})</td>
<td>3.97 \times 10^6</td>
<td>(1.2 \times 10^8)</td>
</tr>
</tbody>
</table>

Avg: \[ 1.7 \times 10^8 \text{ sec}^{-1}(\text{molec/cm}^3)^{1/2} \]
of 3000°K fits the lower pressure spectrum fairly well, but is somewhat too high for the higher pressure spectrum.

Though the choice of rotational temperature does affect vibrational populations slightly at a given pressure, it has no effect in kinetic data because the behavior of the population of a certain vibrational level versus pressure is not affected. From the figures shown and other experiments it was determined that a rotational temperature of 1500°K came closest to fitting the most data, so 1500°K was chosen as the standard and used for all experiments. This temperature was found to persist to the high pressure end of these experiments, though the high pressure was 0.1 Torr at the most.

A temperature of 1500°K is quite high, but not unexpected at the low pressures of these experiments. For instance at 5×10⁻² Torr, an excited hydroxyl radical is expected to undergo 300-500 collisions during its lifetime. Comparison of Figs 15 and 16 show that rotational relaxation is indeed occurring. Murphy,⁴⁶ working at pressures two orders of magnitude higher, measured rotational temperatures of approximately 550°K. In observing infrared chemiluminescence from HCl at a total pressure of 1.8 Torr, Polanyi⁴⁸ found that a temperature of approximately 2000°K best described the rotational distribution.

D. Reaction Rate Constants for Hydroxyl Plus Ozone

These experiments were carried out as described in the experimental section and analyzed as described in Section III D.2. The final steady state equation chosen to determine these rate constants was
Fig. 15a. Hydroxyl spectrum at $1.1 \times 10^{-3}$ Torr total pressure.
Fig. 15b. Hydroxyl spectrum at $1.9 \times 10^{-3}$ Torr total pressure.
Fig. 16a. Hydroxyl spectrum at $12 \times 10^{-13}$ Torr total pressure.
RUN II 3000°K

- - - - CALCULATED
- - - - OBSERVED

Fig. 16b. Hydroxyl spectrum at 12×10⁻³ Torr total pressure.
The parameter \( x(3) \) is the quantity of interest, \( k_v^2 \). Parameter \( x(4) \) is the concentration proportionality factor which was held at a value of \( 1.0 \times 10^6 \). Since hydroxyl concentrations, expressed in relative terms, were about \( 5 \times 10^4 \) this hydroxyl self-reaction factor was very small. Parameter \( x(5) \) is the wall quenching constant which was held at \( 1.7 \times 10^8 \). Parameters \( x(1) \) and \( x(2) \) being in the numerator are measures of the rate of production of hydroxyl. Because these processes could not be measured, \( x(1) \) and \( x(2) \) were allowed to vary. Thus there are three parameters to be fitted and in these experiments the number of data sets ranged from six to sixteen. The results for these experiments are shown in Table XII. These results and those of Worley and co-workers\(^9\) are shown in Fig. 17. The rate constants found in this work are almost uniformly 40% higher than those of Worley. This difference can easily be attributed to the high rotational temperature present in this work. The high rotational temperature means that the average energy within a given vibrational manifold is increased. Since the rate constant is shown to be energy dependent, an increase in average energy would be expected to increase the rate constant.
Table XII. Rate Constants for Reaction of H0(v) + O₃

\[ k^v \times 10^{12} \text{ (cm}^3\text{/molecule-sec)} \]

<table>
<thead>
<tr>
<th>Exp ( v )</th>
<th>9</th>
<th>8</th>
<th>7</th>
<th>6</th>
<th>5</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>11</td>
<td>9.4</td>
<td>8.6</td>
<td>7.4</td>
<td>4.6</td>
<td>3.8</td>
</tr>
<tr>
<td>2</td>
<td>11</td>
<td>9.0</td>
<td>8.8</td>
<td>7.2</td>
<td>4.5</td>
<td>3.8</td>
</tr>
<tr>
<td>3</td>
<td>10</td>
<td>8.5</td>
<td>8.2</td>
<td>6.8</td>
<td>4.3</td>
<td>3.5</td>
</tr>
<tr>
<td>4</td>
<td>11</td>
<td>8.7</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>12</td>
<td>8.9</td>
<td>8.3</td>
<td>7.1</td>
<td>4.7</td>
<td>3.7</td>
</tr>
</tbody>
</table>

Avg: 11 8.9 8.5 7.1 4.5 3.7

Mean Deviation: ±.40 ±.24 ±.23 ±.18 ±.13 ±.10
This Work


Fig. 17.
The reaction of HO and O₃ can lead to a variety of products. The choice of reaction path may be mirrored in the behavior of the rate constant and it also adds complications to determining the rate constant.

\[
\begin{align*}
H + O₂ + O₂ \quad (v>1) \\
HO(v) + O₃ \rightarrow HO + O₂ + O \quad (v>3) \\
HO₂ + O₂ \quad (v>0)
\end{align*}
\]

The first reaction produces secondary hydrogen atoms which may in turn react with ozone to produce more excited hydroxyl radicals. If this path is important and not compensated for in the kinetic model, the rate constants determined would be low. As described in section III D.2, this reaction path was compensated for by parameter x(2) which is an "average" rate constant for HO(v=4-9), reacting to produce secondary H atoms. Because the value of this parameter comes as a result of a fit to experimental data, naturally it varies from one experiment to the next, but it typically had a value of close to \(5 \times 10^{-13} \text{ cm}^3/\text{molec-sec}\). One cannot attach any significance to the number beyond noting that it seems to indicate that the reaction to produce secondary hydrogen is not particularly favored.

As seen in Fig. 17, there is a dramatic jump in \(k_2\) between \(v=5\) and \(v=6\). This is most probably due to the onset of the second reaction. The existence of another reaction channel which becomes energetically favorable would certainly increase the total rate constant.
As a measure of the validity of the steady state model and of the parameters determined by that model, it is necessary to examine the goodness of the fit. The function to be minimized was the sum of the squares of the differences between an observed HO population and a calculated HO population. Table XIII shows some of the values relating to the fit for a typical experiment. Noting the figures in the last row, we see that this model (3 parameters) was able to fit sixteen different populations observed at pressures from $1.0 \times 10^{-3}$ Torr to $2.4 \times 10^{-2}$ Torr within an average of less than four percent. This result seems to validate both the model and the results.

Anderson and Kaufman\(^4^9\) give a value of $5 \times 10^{-14}$ cm\(^3\)/molec-sec for HO\((v=0) + O_3 \rightarrow HO_2 + O_2\) at room temperature. An extrapolation of the present data to \(v=0\) is not easy. If only the results for \(v=4\) and \(v=5\) are extrapolated to \(v=0\), we obtain a value of $5 \times 10^{-13}$ cm\(^3\)/molec-sec. This may not be unreasonable because the values for \(v=4\) and 5 are based on an elevated rotational temperature and presumably two possible reaction channels. Kaufman's value at \(v=0\) is based on low rotational temperature and only one reaction channel.

E. Results for Quenching HO\((v)\), \(v=4-9\)

These experiments were all done in identical fashion, the intensity of emission at a given wavelength was observed as the amount of M gas was slowly increased. The pressure range of the experiments was typically $1 \times 10^{-3}$ to $1 \times 10^{-1}$ Torr. The results were analyzed as described in section III D. 2. Equation (22) of that section was used to determine the quenching constants.
Table XIII. \( \text{HO} + \text{O}_3 \) 1/31/74 16 pts.

<table>
<thead>
<tr>
<th>( v )</th>
<th>( x(1) )</th>
<th>( x(2) )</th>
<th>( x(3) = k )</th>
<th>( x(4)^+ = \text{FCONC} )</th>
<th>( x(5)^+ = \text{RWALL} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( x(1) )</td>
<td>( 1.3 \times 10^7 )</td>
<td>( 1.2 \times 10^7 )</td>
<td>( 1.7 \times 10^6 )</td>
<td>( 4.7 \times 10^6 )</td>
<td>( 9.4 \times 10^6 )</td>
</tr>
<tr>
<td>( x(2) )</td>
<td>( 4.8 \times 10^{-13} )</td>
<td>( 3.5 \times 10^{-13} )</td>
<td>( 5.3 \times 10^{-13} )</td>
<td>( 3.8 \times 10^{-13} )</td>
<td>( 4.7 \times 10^{-13} )</td>
</tr>
<tr>
<td>( x(3) = k )</td>
<td>( 1.2 \times 10^{-11} )</td>
<td>( 8.9 \times 10^{-12} )</td>
<td>( 8.3 \times 10^{-12} )</td>
<td>( 7.1 \times 10^{-12} )</td>
<td>( 4.7 \times 10^{-12} )</td>
</tr>
<tr>
<td>( x(4)^+ = \text{FCONC} )</td>
<td>( 1.0 \times 10^6 )</td>
<td>( 1.0 \times 10^6 )</td>
<td>( 1.0 \times 10^6 )</td>
<td>( 1.0 \times 10^6 )</td>
<td>( 1.0 \times 10^6 )</td>
</tr>
<tr>
<td>( x(5)^+ = \text{RWALL} )</td>
<td>( 1.7 \times 10^8 )</td>
<td>( 1.7 \times 10^8 )</td>
<td>( 1.7 \times 10^8 )</td>
<td>( 1.7 \times 10^8 )</td>
<td>( 1.7 \times 10^8 )</td>
</tr>
</tbody>
</table>

\(^{+}\)held constant

| \( \Sigma \Delta^2 \) | \( 1.5 \times 10^7 \) | \( 1.3 \times 10^7 \) | \( 7.9 \times 10^6 \) | \( 8.0 \times 10^6 \) | \( 6.5 \times 10^7 \) | \( 6.6 \times 10^7 \) |
| Avg. \( \Delta \) | 955 | 915 | 704 | 707 | 2011 | 2029 |
| Avg. obs. pop. | \( 2.14 \times 10^4 \) | \( 2.31 \times 10^4 \) | \( 1.99 \times 10^4 \) | \( 2.16 \times 10^4 \) | \( 4.30 \times 10^4 \) | \( 9.24 \times 10^4 \) |
| Avg. \% deviation | 4.5 | 4.0 | 3.5 | 3.3 | 4.7 | 2.2 |
1. Quenching with Argon

Quenching with argon was investigated because Ar is often used as an M gas in reaction systems to raise the pressure to retard diffusion and quenching at the walls. Because with Ar, only vibration-translation (V-T) energy transfer may occur, and as this process is expected to be slow, an excess of Ar is usually said to have no effect on the system.

Only two experiments were carried out with Ar, one covering $v=8$ and $9$ and one covering $v=4-9$. For the first experiment the results are $k_q^9 = 1.6 \times 10^{-13}$ cm$^3$/molec-sec and $k_q^8 = 2.4 \times 10^{-13}$ cm$^3$/molec-sec. The other results are shown in Table XIV and Fig. 18. Because only two vibrational levels were determined by both experiments, it is not significant to average the results. The results do demonstrate that quenching with argon is much slower than reaction and slower, as will be seen, than quenching with other species. However rate constants close to $10^{-13}$ cm$^3$/molec-sec are by no means extremely slow. These results indicate that Ar is not necessarily inert with respect to quenching, and its effect on the system should not be ignored.

The average percent deviation, shown in Table XIV, shows that the model fits less well for the lower vibrational levels and therefore there is accompanying greater uncertainty in the values of $k_q$. This trend is common to all the quenching experiments carried out.

2. Quenching with Oxygen

Two complete experiments were carried out with $O_2$ as a quenching gas and the results are summarized in Table XV and Fig. 19. The closeness of fit to the model follows the trend noted in the previous section. The average percent deviation behaves as follows.
Table XIV. Results for Quenching H\(_2\)O(v) with Argon

<table>
<thead>
<tr>
<th>(k_q (\text{cm}^3/\text{molec-sec}))</th>
<th>9</th>
<th>8</th>
<th>7</th>
<th>6</th>
<th>5</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1×10(^{-13})</td>
<td>1.1×10(^{-13})</td>
<td>2.2×10(^{-13})</td>
<td>2.9×10(^{-13})</td>
<td>1.5×10(^{-13})</td>
<td>7.9×10(^{-15})</td>
<td></td>
</tr>
<tr>
<td>(\Sigma \Delta^2)</td>
<td>7.1×10(^5)</td>
<td>8.9×10(^6)</td>
<td>2.5×10(^7)</td>
<td>2.1×10(^7)</td>
<td>1.1×10(^8)</td>
<td>1.1×10(^9)</td>
</tr>
<tr>
<td>Avg. (\Delta)</td>
<td>200</td>
<td>720</td>
<td>1.2×10(^3)</td>
<td>1.1×10(^3)</td>
<td>2.5×10(^3)</td>
<td>8.1×10(^3)</td>
</tr>
<tr>
<td>Avg. obs. pop.</td>
<td>1.1×10(^4)</td>
<td>1.6×10(^4)</td>
<td>9.3×10(^3)</td>
<td>6.7×10(^3)</td>
<td>1.2×10(^4)</td>
<td>6.4×10(^4)</td>
</tr>
<tr>
<td>Avg. % dev.</td>
<td>1.9</td>
<td>4.6</td>
<td>13.1</td>
<td>16.1</td>
<td>20.9</td>
<td>12.6</td>
</tr>
</tbody>
</table>
Fig. 18. HO(v) + Ar Quenching Rate Constants.
Table XV. Results for Quenching HO(v) with Oxygen

\[ k_q \times 10^{13} \text{ (cm}^3/\text{molecule-sec)} \]

<table>
<thead>
<tr>
<th>Exp ( v )</th>
<th>9</th>
<th>8</th>
<th>7</th>
<th>6</th>
<th>5</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.4</td>
<td>5.8</td>
<td>7.7</td>
<td>6.7</td>
<td>2.9</td>
<td>1.4</td>
</tr>
<tr>
<td>2</td>
<td>3.6</td>
<td>4.9</td>
<td>7.9</td>
<td>7.8</td>
<td>3.4</td>
<td>1.3</td>
</tr>
<tr>
<td>Avg.</td>
<td>3.5</td>
<td>5.4</td>
<td>7.8</td>
<td>7.3</td>
<td>3.2</td>
<td>1.4</td>
</tr>
</tbody>
</table>
Fig. 19 HO(v) + O₂ Quenching Rate Constants.
3. **Quenching with Nitrogen**

Quenching HO(v) with N₂ as an M gas was studied very thoroughly. The final results are summarized in Table XVI and Fig. 20. The deviations listed here are merely a measure of the precision of the experiments, though the increasing deviation at low v is expected. A check of the goodness of the fit, i.e., how well a set of populations calculated with these rate constants compares to an observed set of populations reveals the following.

<table>
<thead>
<tr>
<th>Average % deviation</th>
<th>9</th>
<th>8</th>
<th>7</th>
<th>6</th>
<th>5</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2.9</td>
<td>7.2</td>
<td>7.3</td>
<td>20.6</td>
<td>13.0</td>
<td>14.5</td>
</tr>
</tbody>
</table>

The average percent deviation is calculated by dividing the average deviation, derived from the sum of the squares of the residuals, by an average observed population.

\[
\text{Avg} \% \text{ dev.} = \left( \frac{\sum_{N} [\text{HO}]_{\text{calc}} - [\text{HO}]_{\text{obs}}}{N} \right)^{1/2} + \frac{\sum_{N} [\text{HO}]_{\text{obs}}}{N}
\]

where N is the number of observations, each at a different pressure.

4. **Quenching with Hydrogen**

Hydrogen is an interesting species to use as a quenching gas because of its low mass and high vibrational frequency. The efficiency of V-T and V-V energy transfer is expected to depend on the reduced mass.
Table XVI. Results for Quenching HO(v) with Nitrogen

\[ k_q \times 10^{13} \text{ (cm}^3/\text{molecule-sec)} \]

<table>
<thead>
<tr>
<th>Exp \ v</th>
<th>9</th>
<th>8</th>
<th>7</th>
<th>6</th>
<th>5</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.8</td>
<td>3.1</td>
<td>7.3</td>
<td>4.9</td>
<td>2.3</td>
<td>.98</td>
</tr>
<tr>
<td>2</td>
<td>5.5</td>
<td>4.0</td>
<td>3.6</td>
<td>8.2</td>
<td>.67</td>
<td>1.5</td>
</tr>
<tr>
<td>3</td>
<td>6.2</td>
<td>4.2</td>
<td>3.1</td>
<td>2.3</td>
<td>1.2</td>
<td>.71</td>
</tr>
<tr>
<td>4</td>
<td>5.7</td>
<td>4.8</td>
<td>5.6</td>
<td>5.2</td>
<td>3.9</td>
<td>1.4</td>
</tr>
<tr>
<td>5</td>
<td>4.4</td>
<td>4.0</td>
<td>6.6</td>
<td>4.4</td>
<td>2.1</td>
<td>.40</td>
</tr>
<tr>
<td>6</td>
<td>3.6</td>
<td>3.0</td>
<td>8.0</td>
<td>6.2</td>
<td>2.7</td>
<td>.20</td>
</tr>
<tr>
<td>7</td>
<td>1.8</td>
<td>2.8</td>
<td>4.4</td>
<td>3.5</td>
<td>1.5</td>
<td>.05</td>
</tr>
<tr>
<td>Avg.</td>
<td>4.4</td>
<td>3.7</td>
<td>5.5</td>
<td>5.0</td>
<td>2.1</td>
<td>.78</td>
</tr>
</tbody>
</table>

Mean Deviation ±1.2 ± .63 ±1.6 ±1.4 ± .80 ±.49

% Mean Deviation ±27 ±17 ±24 ±28 ±38 ±63
Fig. 20. HO(v) + N₂ Quenching Rate Constants.
and relative vibrational frequencies of the colliding partners, so an experiment with hydrogen should point up any observable trends. The results for quenching with $H_2$ are presented in Table XVII and Fig. 21.

The average percent deviation in fitting the experimentally observed populations is quite good as shown below.

<table>
<thead>
<tr>
<th></th>
<th>9</th>
<th>8</th>
<th>7</th>
<th>6</th>
<th>5</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average % deviation</td>
<td>8.4</td>
<td>8.6</td>
<td>7.0</td>
<td>6.9</td>
<td>8.5</td>
<td>13.8</td>
</tr>
</tbody>
</table>

An interesting question which may be raised at this point is whether $H_2$ is reacting with $HO(v)$. The rate constant for $HO(v=0) + H_2 \rightarrow H_2O + H$ has been measured at room temperature by Stuhl and Niki. They report a value of $7.1 \times 10^{-15}$ cm$^3$/molec·sec. As it does with $O_3$, $HO(v>0)$ might be expected to react much faster with $H_2$ than would $HO(v=0)$. However several pieces of evidence, none of which is absolutely conclusive by itself, point to a conclusion that if $HO(v>0)$ does react faster with $H_2$ it is not sufficiently fast to compete with quenching.

A comparison of the 4-0 band in Figs. 15a and 16a, shows that there is an initial rise in intensity as pressure is increased ($1.1 \times 10^{-3}$ Torr and $12 \times 10^{-3}$ Torr, respectively). This rise is most pronounced in the lower $v$ states ($v=4,5$) and nonexistent for state $v=9$. This initial rise in population is due to the state being populated faster by quenching from the state above than it is being depopulated by quenching. This phenomena was observed to be of nearly equal magnitude for all quenching experiments done with $H_2$, $N_2$ or $O_2$ whereas it was
Table XVII. Results for Quenching HO(v) with Hydrogen

<table>
<thead>
<tr>
<th>Exp \ v</th>
<th>9</th>
<th>8</th>
<th>7</th>
<th>6</th>
<th>5</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6.6</td>
<td>6.8</td>
<td>9.0</td>
<td>7.3</td>
<td>5.1</td>
<td>1.8</td>
</tr>
<tr>
<td>2</td>
<td>6.1</td>
<td>5.3</td>
<td>4.4</td>
<td>4.0</td>
<td>3.0</td>
<td>1.4</td>
</tr>
<tr>
<td>3</td>
<td>5.8</td>
<td>3.9</td>
<td>4.7</td>
<td>4.8</td>
<td>3.1</td>
<td>2.4</td>
</tr>
<tr>
<td>4</td>
<td>5.6</td>
<td>14</td>
<td>11</td>
<td>9.8</td>
<td>4.4</td>
<td>1.1</td>
</tr>
<tr>
<td>5</td>
<td>4.8</td>
<td>7.2</td>
<td>11</td>
<td>9.2</td>
<td>4.5</td>
<td>2.5</td>
</tr>
<tr>
<td>Avg.</td>
<td>5.8</td>
<td>7.4</td>
<td>8.0</td>
<td>7.0</td>
<td>4.0</td>
<td>1.8</td>
</tr>
</tbody>
</table>

$k_q \times 10^{13}$ (cm$^3$/molecule-sec)

Mean Dev. $\pm 0.46 \pm 2.6 \pm 2.8 \pm 2.1 \pm 0.78 \pm 0.48$

% Mean Dev. $\pm 7.9 \pm 35 \pm 35 \pm 30 \pm 20 \pm 27$
Fig. 21. HO(v) + H$_2$ Quenching Rate Constants.
not observed when measuring a known reaction, such as the reaction with ozone.

Another indication is that populations computed according to the quenching model fit the observed populations quite well, better in fact than the fit when quenching with N₂. The quenching model specifically requires each state to be quenched to the next lower state and this in fact is the dominant path by which the lower states are populated. Any HO(v) that reacts would be removed from the manifold of states and this would result in a poorly fitting model.

Finally if HO(v) were to react with H₂, a secondary hydrogen atom would be produced which would in turn react to produce a new excited hydroxyl. This would have the effect of reducing the apparent rates for the higher v states which are significantly populated by reaction and would have an uncertain effect on the lower v states depending upon the competition between reaction or quenching with H₂. A method investigating this possibility is to study HO(v) + D₂.

If HO(v) were to react with D₂, the free D atom would then react with O₃ and produce an excited DO molecule. This latter reaction is 77.8 kcal/mole exothermic which is enough energy to populate up to v=12 of the ground electronic state. Eighteen bands of DO emission (Δv=5,6,7,8,9) fall in the region of the spectrum which was observed, roughly 12,000 cm⁻¹ to 18,000 cm⁻¹. Unfortunately emission intensity in any of these bands would be expected to be quite low because of the decreasing transition probability with increasing Δv.
Several experiments were performed with $D_2$ as a quenching gas for $HO(v)$ and the rate constants for these processes will be presented in the next section. On several carefully recorded spectra, no evidence was found for any emission from vibrationally excited DO.

From the several pieces of evidences, it is concluded that $HO(v)$ reacting with $H$ is not fast enough to compete with the quenching processes.

5. Quenching with Deuterium

The experiment with deuterium was of interest for several reasons. Looking for emission from DO as an indicator for the $HO(v) + H_2$ reaction was described in the previous section. The rate constants for $HO(v)$ being quenched by $D_2$ might also serve to establish quenching probability trends based on mass or vibrational frequency which can be explained by current energy transfer theory.

The results for $D_2$ are summarized in Table XVIII and Fig. 22. The average percent deviation of the model from the experimentally observed populations is given below.

<table>
<thead>
<tr>
<th>Average % deviation</th>
<th>9</th>
<th>8</th>
<th>7</th>
<th>6</th>
<th>5</th>
<th>4</th>
</tr>
</thead>
</table>

That $k^9$ is slower for $D_2$ than $H_2$ also seems to indicate no significant reaction of $HO(v)$ with $H_2$ or $D_2$ is occurring. If those reactions were to occur, the reaction with $H_2$ would slow the apparent rate constant while the reaction with $D_2$ would not affect it. The results do not lend any support to this possibility.
Fig. 22. HO(v) + D₂ Quenching Rate Constants.
Table XVIII. Results for Quenching HO(v) with Deuterium

\[
k_q \times 10^{13} \text{ (cm}^3/\text{molecule-sec)}
\]

<table>
<thead>
<tr>
<th>Exp \ v</th>
<th>9</th>
<th>8</th>
<th>7</th>
<th>6</th>
<th>5</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.8</td>
<td>6.3</td>
<td>9.5</td>
<td>8.3</td>
<td>3.9</td>
<td>1.7</td>
</tr>
<tr>
<td>2</td>
<td>4.9</td>
<td>6.5</td>
<td>12</td>
<td>9.0</td>
<td>4.7</td>
<td>2.3</td>
</tr>
<tr>
<td>Avg.</td>
<td>4.9</td>
<td>6.4</td>
<td>11</td>
<td>8.6</td>
<td>4.3</td>
<td>2.0</td>
</tr>
</tbody>
</table>
V. VIBRATIONAL ENERGY TRANSFER

In this chapter vibrational energy transfer theory and experiments which may be compared to or contrasted with these results for the hydroxyl radical will be reviewed and discussed. Features which may point toward an explanation of the behavior found here for the hydroxyl radical will be highlighted.

A. Review of Selected Energy Transfer Theories and Experiments

There is a large and ever increasing literature trying to explain vibrational energy transfer, but it is primarily focussed on the lowest vibrational states. However the recent interest in the chemical laser has brought forth some experiments and calculations on energy transfer processes in higher vibrational levels.

Two major types of vibrational energy transfer processes may occur. In vibrational-translational (V-T) transfer a diatomic molecule with excess vibrational energy collides with an atom and transfers one or more quanta of energy to it. Because the atom has only translational degrees of freedom, all the energy transferred must be converted to translation. Since this amount of energy is usually much larger than kT, the transfer probability is very small.

In vibrational-vibrational transfer (V-V) the diatomic molecule collides with another diatomic or polyatomic molecule. Because there are now vibrational degrees of freedom to transfer energy into, it is assumed that as much energy as possible is transferred from vibration to vibration and any remaining energy of the first molecules vibrational
quantum (the energy defect) is converted to translation of the collision partner. Though dependent upon the efficiency of the V-V transfer and the size of the energy defect, the transfer probability is expected to be much larger than for a V-T process.

1. V-T Energy Transfer

The development of V-T energy transfer theory and the many varieties of classical, semi-classical, and quantum calculations are presented in a review by Rapp and Kassal.\textsuperscript{52} The most commonly referenced theory is the first order distorted wave treatment of Schwartz, Slawsky, and Herzfeld (SSH).\textsuperscript{53,54} This is an approximate quantum calculation in which the total wave function is approximated by a large term composed of elastically scattered states and a small term of inelastically scattered states. The interaction between A and BC is assumed to be an exponential repulsion.

Several general predictions of this theory should be noted. First, transition probabilities calculated at room temperature are very small, ranging from $10^{-4}$ to $10^{-9}$ or less for different molecules. This is mainly due to the destructive overlap of the initial and final translational wavefunctions. Transition probabilities are expected to increase as the relative velocity of the collision partners increases or as the reduced mass of the collision partners decreases. For both harmonic and anharmonic oscillators, transitions with $\Delta v=1$ are far more probable than multiquantum transitions. The matrix elements for single quantum transitions are larger, but more important, the translational overlap is even smaller if more than one quantum of energy must be converted from vibration to translation.
Finally, transition probabilities are expected to increase as the vibrational quantum number of BC increases. For harmonic oscillators $P_{v \rightarrow v-1} = vP_{1 \rightarrow 0}$. For an anharmonic oscillator the probability might be expected to increase even faster because of the decrease in the size of the vibrational quantum as $v$ increases.

In comparison with experiment, the SSH theory has shown moderate success, but often predicts probabilities one to two orders of magnitude less than experimental values.\textsuperscript{22,52}

Kajimoto and Fueno\textsuperscript{55} have done an exact classical mechanical calculation for an atom striking an anharmonic (Morse) diatomic molecule with an exponential repulsive potential of interaction. At low vibrational levels, their calculations agree quite well with the exact quantum calculation of Secrest and Johnson.\textsuperscript{56} As expected they find that transitions become more efficient with an increase in initial vibrational energy, but in the high vibrational energy region they find a maximum and then a decrease in energy transfer efficiency as the dissociation limit is approached. This calculation is of interest because it raises the possibility that energy transfer probability is not a simple monotonically increasing function of vibrational level.

A few experiments have been reported in which an atom deactivates a vibrationally excited diatomic molecule very efficiently. Breshears and Bird\textsuperscript{57} report a chemical effect in an investigation of the vibrational relaxation of $N_2$ by atomic oxygen. In a shock tube experiment, Kiefer and Lutz\textsuperscript{58} found that the presence of a small amount of oxygen atoms significantly increased the relaxation rate of vibrationally excited
Such energy transfer effects as low reduced mass vibration-rotation transfer, or resonant vibrational transfer obviously cannot be significant in this case, so it should be an unambiguous example of a chemical effect. What is meant by a chemical effect is that a minimum exists in the interaction potential between A and BC. The minimum may exist because A and BC do in fact react to form a stable molecule, as is the case of oxygen atoms and oxygen molecules, or there may be some metastable intermediate complex in a situation such as an atom exchange reaction, or there may be some non-reactive interaction such as hydrogen bonding. The depth of the minimum in the interaction potential would vary in each of these cases, but the effect in each case would be to increase the efficiency of energy transfer either by trapping a bound complex in the well for a few vibrational periods or by favorably orienting the molecules during the collision.

Simple one dimensional semiclassical theory predicts a high probability and very slight energy dependence for vibrational transfer when a model with a deep minimum in the interaction potential is used. This observation is important because it points up the possibility of efficient energy transfer even though there is a large energy defect: something the SSH theory does not predict.

Breig has done statistical analysis of classical trajectories for the deactivation of molecular by atomic oxygen. The actual form of the interaction potential between an oxygen atom and an oxygen molecule is unknown, but the stability of ozone suggests a deep minimum in the intermolecular potential. The principal portion of the intermolecular
potential for this problem was chosen to be a sum of Morse potentials for each pair of particles in the system. The well in which the three particle intermediate complex formed was modelled to be 1.04 eV deep. This attractive potential is in contrast to the normal van der Waal attractions which are on the order of 0.01 eV. With this model, Breig calculated cross sections for energy transfer of the same order as gas kinetic cross sections. For a potential well of 0.1 eV, cross sections were lower by a factor of four to an order of magnitude but a cross section of one-tenth gas kinetic is still very large.

In analyzing individual trajectories, Breig found a high probability that the intermediate complex existed for several vibrational periods. When this happens the probability of multiquantum transitions is quite large because there is sufficient time for the energy of the vibrating diatomic to be redistributed over the entire intermediate complex.

2. V-V Energy Transfer

For a long period of time, molecular vibration was treated as adiabatic with respect to long range forces, so the theory of V-V exchange was built on calculations with a short range exponential repulsion as the only intermolecular potential responsible for energy transfer. The SSH theory was extended to included V-V transfer between two diatomic molecules. This theory calculates largest probabilities for single quantum V-V exchange at exact resonance and very steeply decreasing probabilities for exchange with an increasing energy defect. It has had some success in predicting energy transfer rates for non-hydride molecules, but it is consistently unable to account for
the high probabilities measured in experiments with CO$_2$ and hydrogen halides. A very similar semiclassical calculation by Rapp and Englander-Golden$^{62}$ suffers the same inadequacy.

Sentman$^{63}$ has expanded on the model of Rapp and Sharp$^{64}$ and Rapp and Englander-Golden by including vibration-rotation as a mode of energy transfer for the relaxation of hydrogen halides. This improves predicted probabilities somewhat, but most of his calculations remain nearly an order of magnitude below experimental values.

Stettler and Witrict$^{65}$ do a short range forces calculation using the impact parameter version of the Born approximation$^{66}$ rather than the distorted wave version used in the SSH theory. This approximation considers only collisions with large impact parameters, so the molecules are assumed to move classically along straight line paths. For collisions of this sort, transition probabilities are small enough that the problem may be treated by first order perturbation theory. The estimated probabilities calculated for selected cases, were always greater than those predicted by SSH theory and for HCl and HBr self deactivation were close to experimentally measured values.

In a break from the previous calculations emphasizing V-V energy transfer due to short range repulsive interactions, Mahan$^{67}$ suggests that resonant V-V exchange may be due to long range dipole-dipole interactions in infrared active molecules. Mahan uses the impact parameter approximation and assumes that for an impact parameter $b$ less then some value $b_c$, the probability of vibrational exchange is one-third.
For impact parameters within the range of his theory, i.e. \( b \gg b_c \), Mahan calculates energy exchange cross sections as great as 0.01 or 0.1 times as large as gas kinetic cross sections. These are at least ten times faster than calculations using the short range potential.

The idea of long range interaction has been further developed by Sharma. 68-70 He has calculated rates for V-V exchange under the influence of dipole-dipole coupling, but has specifically looked into the influence of higher order multipole coupling and the role of vibration-rotation-translation exchange in near-resonant processes. He has been quite successful in calculating V-V rates for \( \text{CO}_2 \) isotopes by dipole-octupole coupling, for \( \text{CO}_2 \) to \( \text{N}_2 \) exchange by dipole-quadrupole coupling, and for \( \text{CO} \) to \( \text{H}_2 \) exchange by dipole-hexadecapole coupling. In all of these cases the strict dipole-dipole selection rule that \( \Delta J = \pm 1 \) is relaxed and it is found that rotation serves as a buffer to absorb or lend a small amount of energy to lessen the vibrational energy defect. This serves to soften the resonance requirements and greatly increase the cross sections over a small range of energy defect.

The effect of long range interaction has also been extended to nonresonant V-V transfer in a simple dipole-dipole model by Yardley 71 and in an extension of the Sharma-Brau multipole theory 69 by Tam. 72 Tam's calculations were applied to the chemiluminescence experiments of Hancock and Smith 22 on \( \text{CO}(v \leq 12) \) deactivated by \( \text{CO}(v=0) \). The agreement was quite good except for \( v=11 \) and 12, the states for which the energy defect is largest, so there is still some weakness in the
theory for considerably non-resonant exchanges.

In summary, the long range interaction theories relying on a Born approximation have been quite successful in calculating resonant and near resonant V-V energy transfer, with less success as the energy defect increases. The theory has accounted for very large cross sections, approximately gas kinetic in exchange between CO₂ isotopes. The general predictions of the theory are very high probabilities of exchange at and near resonance and sharply decreasing probabilities as the energy defect increases far from resonance. Jeffers and Kelley⁷³ made the logical next step of calculating V-V transition probabilities due to both long range and short range forces. They also compare their calculations to the data of Hancock and Smith and are able to match this data at 300°K to within twenty-five percent. They find that at this temperature, the short range forces dominate the transition probability for any energy defect greater than 210 cm⁻¹ while long range interactions dominate for smaller energy defects.

Unfortunately this conceptually simple model of adding a short range contribution to a cross section calculated from attractive multipolar forces may not be correct. Dillon and Stephenson investigate the effect of uncertainty in the quantitative expression for short range repulsion.⁷⁷ Whereas multipole potentials can be fairly well defined by spectroscopic or thermodynamic measurements, no quantitative understanding exists for the forces that result from short range overlap of molecular electron distributions. They find that they can nearly reproduce a calculated cross section curve using both high and low values for the parameter
measuring strength of the short range repulsion. Intermediate values have the effect of canceling a significant part of the attractive interaction and drastically reducing the total cross sections. We may conclude from this that the simple additive model is adequate in cases where either long range or short range interactions are dominant, and the cross section resulting from the other interaction is small. Where there may be destructive interference between the short range repulsion and the long range attraction, the simple model is not adequate.

To avoid the strict selection rules of the first Born approximation \((\Delta v=\pm 1, \Delta J=\pm 1)\), and the range of impact parameter for which the approximation is not valid, Dillon and Stephenson have formulated a theory in which they can evaluate all orders of the scattering matrix elements. They use a multipole expansion of the intermolecular potential as in the Sharma-Brau theory. Their calculations for CO vibrational exchange show much less dependence on the energy defect than predicted by the Born approximation. The rates for a \(\Delta v=1\) exchange are an order of magnitude slower near resonance, but seven orders of magnitude or more faster far from resonance. They also calculate the probability of a \(\Delta v=2\) exchange to generally be within an order of magnitude of the \(\Delta v=1\) probability. They conclude that kinetic modelling should possibly be based on the contributions of many small rates of exchange, rather than a few relatively large rates.

In light of recent experiments which measure extremely rapid rates for energy transfer from HF or DF to \(\text{CO}_2\), and which cannot be accounted for by any previously mentioned theory because of the very large energy defect \((1600 \text{ cm}^{-1} \text{ and } 550 \text{ cm}^{-1}, \text{respectively})\), Dillon and
Stephenson have extended and refined their approximate quantum theory to apply to this problem.\textsuperscript{75} They compare their calculations with the experimental data of Airey and Smith\textsuperscript{76} and find agreement within the error estimates of their theory. A very interesting point is that very little of the energy defect between HF($v=1$) and CO\textsubscript{2} went into translation. Their calculations showed that for HF an initial rotational state $J=2$ and a final rotational state $J=9$ was most probable.

The vibrational relaxation of the hydrogen halides has also been modelled in a classical calculation by H. K. Shin.\textsuperscript{78} His model is that of a rotation averaged vibrator, or "breathing sphere" colliding with a rigid rotator under the influence of a potential which is the sum of exponential interactions (Morse potential type) between the atoms of the different molecules. Shin finds that the dominant mode of energy transfer is vibration-rotation transfer taking place through the interaction of the two hydrogen atoms. The expected large attractive interactions such as dipole-dipole or hydrogen bonding are not important because they represent interaction between the hydrogen atom on one molecule and halide atom on the other. His calculated results agree quite well with experimental results for hydrogen halide (HCl, HBr, and HI) self relaxation.

However to attempt to match experimental data on HF or DF relaxation, it is necessary to modify this theory. Experimental measurements on HF are moderately well matched if an attractive potential of about 3 kcal/mole (hydrogen bonding) is added to the theory.\textsuperscript{79} Conceptually,
this attractive potential is supposed to accelerate the colliding molecules towards one another, thereby increasing the relative velocity at which the hydrogen atoms strike each other. Unfortunately neither the basic theory nor the modified theory satisfactorily explain the experimental results for DF relaxation. 

An area of speculation for V-V transfer is the existence and significance of strong attractive forces such as HF dimer formation or hydrogen bonding (estimated well depth of 2-4 kcal/mole). There seems little doubt that an attractive potential, whether it is responsible for a very temporary intermediate complex, for favorably orienting the molecular axes of collision partners, or only for causing the colliding molecules to travel on curved trajectories, would significantly increase the efficiency of V-V energy transfer. Several researchers\textsuperscript{76, 81-83} have pointed to attractive potentials as a possible explanation for very high rates of V-V transfer. This hypothesis may be supported by noting the inverse temperature dependence, at low temperatures, of HF and DF relaxation. The efficiency of an attractive potential is expected to increase with decreasing relative translational energy or temperature.

B. Energy Transfer in Vibrationally Excited HO

A simple prediction and explanation for the behavior of excited HO may be inferred from the following general comparison.
<table>
<thead>
<tr>
<th></th>
<th>CO</th>
<th>HO</th>
<th>HF</th>
</tr>
</thead>
<tbody>
<tr>
<td>freq.</td>
<td>low vibrational frequency</td>
<td>high vibrational frequency</td>
<td>high vibrational frequency</td>
</tr>
<tr>
<td></td>
<td>small rotational spacing</td>
<td>large rotational spacing</td>
<td>large rotational spacing</td>
</tr>
<tr>
<td>forces</td>
<td>weak attractive forces</td>
<td>strong attractive forces</td>
<td>strong attractive forces</td>
</tr>
<tr>
<td>dipole</td>
<td>dipole moment ≈ 0.1D</td>
<td>dipole moment = 1.7D^84</td>
<td>dipole moment = 1.9D</td>
</tr>
</tbody>
</table>

It is obvious that HO may be expected to show behavior very similar to that of HF, i.e. high rates of vibrational exchange probably influenced by an attractive potential with a shallow well in it.

A comparison of some experimental results obtained by similar experimental technique for all three molecules, also serves to place hydroxyl quenching behavior close to that of HF. Measured rate constants for quenching CO(4≤ν≤13)^22 with a variety of species were typically in the range of $10^{-14} \text{ cm}^3/\text{molecule-sec}$ except for those cases of very near resonant exchange. For HF(ν≤5) being quenched by HF or CO$_2$, rate constants are on the order of $10^{-12} \text{ cm}^3/\text{molecule-sec}$ or faster. The results of this work place the rate constants for HO(4≤ν≤9) near $5\times10^{-13} \text{ cm}^3/\text{molecule-sec}$.

Worley and co-workers^10 have reported rates of interaction for HO(ν=9) plus a variety of M gases. Their measured rate constants (HO(ν=9) + O$_2$, 1.0×10$^{-14}$ cm$^3$/molec-sec; HO(ν=9) + N$_2$, 3.6×10$^{-15}$ cm$^3$/molec-sec) are extremely low and they also report that the rate constant for quenching with O$_2$ is not dependent on HO vibrational level. The low rate constants and lack of dependence on vibrational level are certainly not supported by the expected similarity of HO to HF.
Basov and co-workers\textsuperscript{86} have derived an average value of the rate constant for the transfer of energy from DO\textsuperscript{+} to CO\textsubscript{2} in a CO\textsubscript{2} laser produced by mixing O\textsubscript{3}, D\textsubscript{2}, and CO\textsubscript{2}. Their value is $$(5\pm2.5)\times10^{-13}$$ cm\textsuperscript{3}/molec-sec. Since DO\textsuperscript{+} should be quenched faster than HO\textsuperscript{+}, this value might seem low, but Airey and Smith\textsuperscript{76} note that the Basov value for DF\textsuperscript{+} deactivation is also low. Even if this value is not low, it is more than an order of magnitude higher than the value reported by Worley et al. for the process HO(v=9) + CO\textsubscript{2}.

With the evidence that HO is expected to be quenched very efficiently by other diatomics, it is interesting to note that quenching by Ar, while certainly not as efficient, is not reduced by the several orders of magnitude expected when there is no vibrational degree of freedom into which energy may be transferred. However this is not necessarily an uncommon occurrence. In an experiment on quenching CO(v=1), Stephenson\textsuperscript{87} found that He was more efficient than CO(v=0) and that O\textsubscript{2} was only four times as efficient as He. In a study of quenching of NO\textsubscript{2} fluorescence (electronic excitation) Kaufman and co-workers\textsuperscript{88} found that Ar was more efficient than H\textsubscript{2}, nearly as efficient as N\textsubscript{2} or O\textsubscript{2}, and only 4-6 times less efficient than several polyatomic molecules.

A possible explanation and possibly a significant mechanism in hydroxyl energy transfer is that most or all of the vibrational energy defect is taken up as rotation in one or both of the collision partners. For instance a transition from v=8, J=5/2 to v=7, J=25/2 has an energy defect of only 370 cm\textsuperscript{-1} rather than over 2400 cm\textsuperscript{-1} which is the energy
difference between the rotationless \( v=7 \) and \( v=8 \) levels. In fact higher rotational levels, starting around \( J=27/2 \), begin to overlap the lower rotational levels of the next vibrational state. If the influence of a collision with Ar serves to couple these states, energy transfer could occur with very little energy defect required to go into translation.

An even more striking example of the possible efficiency of rotational excitation in accounting for the energy defect is in quenching \( \text{HO}(v=7) \) with \( \text{N}_2 \). The process

\[
\text{HO}(v=7, J=7/2) + \text{N}_2(v=0) \rightarrow \text{HO}(v=6, J=11/2) + \text{N}_2(v=1) - 18 \text{ cm}^{-1}
\]

requires only \( \Delta J=2 \) for a very near resonant exchange.

A significant aspect of this work was the high rotational temperature exhibited by the hydroxyl radical populations. A rotational temperature of 1500 K means that there was a relatively even distribution of population through all rotational levels up to \( J=25/2 \). This nearly continuous energy spectrum within each vibrational state guarantees the availability of transitions with small energy defects if the traditional selection rules on \( J \) are relaxed. Stephens and Cool also recognize the need for a theory which allows rotational excitation to take up the major portion of the vibrational energy defect. As noted earlier in the theory of Dillon and Stephenson, \( \Delta J=7 \) was the most probable transition in HF deactivation.
The fact that a high rotational temperature was observed in this work for the lower vibrational levels even at the highest pressures used, supports the possibility of rotational excitation during vibrational quenching. The lower vibrational states are populated primarily by quenching and it is expected that rotation should be thermalized very rapidly. There is evidence of rotational relaxation as pressure is increased, so the rotational excitation of the lower vibrational levels may only be the result of relaxation of an even higher initial rotational excitation. Or the continued presence of rotational excitation, even after considerable vibrational quenching of the lower levels, may be the result of rotational excitation during vibrational quenching.

Though the theory of Dillon and Stephenson allows transitions with large $\Delta J$, it is also accepted that energy transfer under the influence of an attractive potential of 'chemical effect' would also remove selection rule restrictions. One such chemical effect is hydrogen bonding. A hydrogen bond is defined loosely as a hydrogen atom already bonded to another atom along with some evidence of a hydrogen bond. This most commonly occurs when a hydrogen atom lies between two closely spaced electronegative atoms, but it has been found to occur, in weaker form, between weakly electronegative atoms. Hydrogen bonding or some form of chemical effect is very likely present in this system in which a free radical (HO) is being vibrationally relaxed by hydrogen, nitrogen, or oxygen. Further evidence for this is the observation that hydrogen molecules were not reacting with vibrationally excited hydroxyl radicals at any significant rate. Polanyi and co-workers
found a relative decrease in the vibrational excitation of the products of an exothermic three atom exchange reaction when the potential surface was made more attractive. This means a highly excited molecule is less likely to undergo the reverse reaction on an attractive potential surface.

Thus it is most likely that hydroxyl radicals are being quenched under the influence of an attractive potential and that a large part of the vibrational energy defect is being taken up as rotational excitation. A theory which incorporates these features should go a long way toward explaining the present results and helping to complete the overall picture of vibrational energy transfer.
ACKNOWLEDGEMENTS

To Professor Harold S. Johnston goes my grateful appreciation for his guidance in the course of this research. His wealth of scientific knowledge and insight has always been present when needed while his philosophy of judicious guidance has allowed me the room to develop my own scientific nature.

I have enjoyed the assistance and encouragement of my fellow graduate students and friends and colleagues and appreciate the many fine discussions we have had about research and the nature of life in Berkeley. I especially thank Dr. Gary Whitten for his able computer programming consultation and for the many close competitive handball games we have enjoyed.

I wish to thank the personnel of the Department of Chemistry and of the Lawrence Berkeley Laboratory who have been most generous and very competent in their support of this research.

Joyful and sincere appreciation goes to my fiance, Gloria, who has provided me with much cherished emotional support and a much needed typewritten copy of my rough draft.

I also thank the National Science Foundation for their support through a Graduate Fellowship and the United States Atomic Energy Commission for their support and for the use of facilities at the Lawrence Berkeley Laboratory.
APPENDIX I. Computer Programs

Routines which are footnoted are standard library routines available at the Lawrence Berkeley Laboratory computation center. Writeups on the routines are available there.

I-A PROGRAM OHSHAPE

This program calculates the band intensities for a synthetic hydroxyl spectrum. It requires input of the vibrational term value (VI), the rotational constant (BV) and the reduced coupling constant (YV) for each vibrational level of the molecule. Also needed are the spectral slit width (SPSW), an assumed rotational temperature (T), the time to scan the spectral slit width (TE), the RC time constant (TAU), and for each band to be calculated, the initial (U) and final (L) vibrational states.

The functions FP3, FQ3,...FRI calculate the frequency in \(\text{cm}^{-1}\) of each line for P,Q or R branches in the 3/2 or 1/2 multiplets given the initial and final vibrational state and a particular J value.

Subroutine PROB reads the transition matrix element (TT) for each band and returns the appropriate value to the main program when needed.

Subroutine SORTR\(^1\) (not listed) orders all the lines within a band in order of increasing wavelength.

The profile of each band is printed out and the same information is stored on a data storage device at the LBL computation center.

\(^1\) Subroutine SORTR, LBL identification M1 BKY SORTR ASCENT F, written by Robert Downs (August, 1966).
PROGRAM OHSHAPE
DIMENSION BV(10), VI(10), YV(10), SJP(2, 20), SJQ(2, 20), SJR(2, 20)
DIMENSION WIS(Z, L), WIS', W(118), SUMA(Z000), LA(Z000)
DIMENSION A(3000, 6)
DIMENSION ZSUM(3000)
INTEGER U, L
REAL J
REAL N
SPEC1(Z)=(Z-1.+EXP(-Z))/TI
SPEC2(Z)=(Z+1.+EXP(-Z))*2.*EXP(-Z))/TI
SPEC3(1)=(Z-1.+EXP(-Z))/TI
CORR(1)=I./(I.+2.68068E-4+1Z**2+3.3E-24*Z**4)
FP31(U, L, J)=VI(U)-VI(L)+BV(U)*((J+1.5)**2+2.5*SQRT(4*(J+1.5)**2+YV(U)*
1(YV(U)-4)))-DV*(J+1)**4-BV(U)*((J+1.5)**2+2.5*SQRT(4*(J+1.5)**2+YV(U)*
2YV(L)-4)))+DV*(J+1)**4-BV(U)+BV(L)
FQ31(U, L, J)=VI(U)-VI(L)+BV(U)*((J+1.5)**2+2.5*SQRT(4*(J+1.5)**2+YV(U)*
1(YV(U)-4)))-DV*(J+1)**4-BV(U)*((J+1.5)**2+2.5*SQRT(4*(J+1.5)**2+YV(U)*
2YV(L)-4)))+DV*(J+1)**4-BV(U)+BV(L)
FR31(U, L, J)=VI(U)-VI(L)+BV(U)*((J-1.5)**2+2.5*SQRT(4*(J-1.5)**2+YV(U)*
1(YV(U)-4)))-DV*(J-1)**4-BV(U)*((J-1.5)**2+2.5*SQRT(4*(J-1.5)**2+YV(U)*
2YV(L)-4)))+DV*(J-1)**4-BV(U)+BV(L)
FPI(U, L, J)=VI(U)-VI(L)+BV(U)*((J-1.5)**2+2.5*SQRT(4*(J-1.5)**2+YV(U)*
1(YV(U)-4)))-DV*(J-1)**4-BV(U)*((J-1.5)**2+2.5*SQRT(4*(J-1.5)**2+YV(U)*
2YV(L)-4)))+DV*(J-1)**4-BV(U)+BV(L)
FR1(U, L, J)=VI(U)-VI(L)+BV(U)*((J+1.5)**2+2.5*SQRT(4*(J+1.5)**2+YV(U)*
1(YV(U)-4)))-DV*(J+1)**4-BV(U)*((J+1.5)**2+2.5*SQRT(4*(J+1.5)**2+YV(U)*
2YV(L)-4)))+DV*(J+1)**4-BV(U)+BV(L)
FR1(U, L, J)=VI(U)-VI(L)+BV(U)*((J+1.5)**2+2.5*SQRT(4*(J+1.5)**2+YV(U)*
1(YV(U)-4)))-DV*(J+1)**4-BV(U)*((J+1.5)**2+2.5*SQRT(4*(J+1.5)**2+YV(U)*
2YV(L)-4)))+DV*(J+1)**4-BV(U)+BV(L)
M=1
CALL PROB(TRAN, TPhOB, M)
DO 4 I=1, 3000
ZSUM(I)=0.0
DO 41 JA=1, 6
A(I, JA)=0.
41 CONTINUE
4 CONTINUE
DV=0.0018
READ1, (VI(I), BV(I), YV(I), I=1, 10)
1 FORMAT(3F12.6)
READ 2, (SJP(I, J), SJQ(I, J), SJR(I, J), J=1, 20), I=1, 2)
2 FORMAT(3F8.4)
READ 3, (SPSW, T, TE, TAU)
3 FORMAT(4F10.3)
PRINT 7, SPSW, T
7 FORMAT(1H1, 19X,*THE FOLLOWING BAND SHAPES ARE FOR A SPECTRAL SLIT
1 WIDTH EQUAL TO*F6.2* ANGSTROMS AND ASSUME*20X,*A ROTATIONAL TEMP
2ERATURE OF*F5.0* DEGREES KELVIN*,
2 PRINT 7, TE, TAU
77 FORMAT(19X*TIME TO SCAN SPECTRAL SLIT WIDTH=**F5.1*SECONDS AT A T
1 ME CONSTANT OF**F5.2*2SECONDS*)
77 TE=TE/TAU
EXTI=EXP(TI)
10 READ II, U, L
11 FORMAT(211)
IF (U.EQ.0) GO TO 400
TRAN=10.*U+L
IF (L.EQ.0) L=10
NL=20
C
IN THE ORDER (P3/2), P1/2, Q3/2), Q1/2), R3/2), K(1/2)
C
EM(1)=EX*FP3(U,L,.5)**3*BV(U)*SJP(1,1)/T
EM(21)=EX*FP1(U,L,.5)**3*BV(U)*SJP(2,1)/T
EM(41)=EX*FO3(U,L,.5)**3*BV(U)*SJO(1,1)/T
EM(61)=EX*FO1(U,L,.5)**3*BV(U)*SJO(2,1)/T
WLAI=1.E8/(FP3(U,L,.5)*CORR(FP3(U,L,.5)))
WLAL=1.E8/(FP1(U,L,.5)*CORR(FP1(U,L,.5)))
WLAI(1)=1.E8/(FP1(U,L,.5)*CORR(FP1(U,L,.5)))
WLAL(2)=1.E8/(FP1(U,L,.5)*CORR(FP1(U,L,.5)))
WLAL(3)=1.E8/(FP1(U,L,.5)*CORR(FP1(U,L,.5)))
WLAL(4)=1.E8/(FP1(U,L,.5)*CORR(FP1(U,L,.5)))
WLAI(1)=1.E8/(FP1(U,L,.5)*CORR(FP1(U,L,.5)))
WLAL(2)=1.E8/(FP1(U,L,.5)*CORR(FP1(U,L,.5)))
WLAL(3)=1.E8/(FP1(U,L,.5)*CORR(FP1(U,L,.5)))
WLAL(4)=1.E8/(FP1(U,L,.5)*CORR(FP1(U,L,.5)))
WLA(5)=1.E8/(FP1(U,L,.5)*CORR(FP1(U,L,.5)))
IF (U.EQ.0) GO TO 400
TRANS=10.*U+L
IF (L.EQ.0) L=10
NL=20
C
IN THE ORDER (P3/2), P1/2, Q3/2), Q1/2), R3/2), K(1/2)
C
EM(1)=EX*FP3(U,L,.5)**3*BV(U)*SJP(1,1)/T
EM(21)=EX*FP1(U,L,.5)**3*BV(U)*SJP(2,1)/T
EM(41)=EX*FO3(U,L,.5)**3*BV(U)*SJO(1,1)/T
EM(61)=EX*FO1(U,L,.5)**3*BV(U)*SJO(2,1)/T
WLAI=1.E8/(FP3(U,L,.5)*CORR(FP3(U,L,.5)))
WLAL=1.E8/(FP1(U,L,.5)*CORR(FP1(U,L,.5)))
WLAI(1)=1.E8/(FP1(U,L,.5)*CORR(FP1(U,L,.5)))
WLAL(2)=1.E8/(FP1(U,L,.5)*CORR(FP1(U,L,.5)))
WLAL(3)=1.E8/(FP1(U,L,.5)*CORR(FP1(U,L,.5)))
WLAL(4)=1.E8/(FP1(U,L,.5)*CORR(FP1(U,L,.5)))
WLAI(1)=1.E8/(FP1(U,L,.5)*CORR(FP1(U,L,.5)))
WLAL(2)=1.E8/(FP1(U,L,.5)*CORR(FP1(U,L,.5)))
WLAL(3)=1.E8/(FP1(U,L,.5)*CORR(FP1(U,L,.5)))
WLAL(4)=1.E8/(FP1(U,L,.5)*CORR(FP1(U,L,.5)))
WLA(5)=1.E8/(FP1(U,L,.5)*CORR(FP1(U,L,.5)))
WLA(61)=1.5/(FP1(U,L,.5)*CORR(FP1(U,L,.5)))
DO 50 K=2,NL
N=K
X=EXP(-EV(U)*((N+.5)*((N+.5)/(.695029*T)))
EM(K)=X*FP3(U,L,.5)**3*BV(U)*SJP(1,K)/T
EM(NL+K)=X*FP1(U,L,.5)**3*BV(U)*SJP(2,K)/T
EM(2*NL+K)=X*FO3(U,L,.5)**3*BV(U)*SJO(1,K)/T
EM(3*NL+K)=X*FO1(U,L,.5)**3*BV(U)*SJO(2,K)/T
EM(4*NL+K)=X*FR3(U,L,.5)**3*BV(U)*SJR(1,K)/T
EM(5*NL+K)=X*FR1(U,L,.5)**3*BV(U)*SJR(2,K)/T
WLAO=1.E8/(FP3(U,L,.5)*CORR(FP3(U,L,.5)))
WLA2=1.E8/(FP1(U,L,.5)*CORR(FP1(U,L,.5)))
WLA3=1.E8/(FP1(U,L,.5)*CORR(FP1(U,L,.5)))
WLA4=1.E8/(FP1(U,L,.5)*CORR(FP1(U,L,.5)))
WLA5=1.E8/(FP1(U,L,.5)*CORR(FP1(U,L,.5)))
WLA6=1.E8/(FP1(U,L,.5)*CORR(FP1(U,L,.5)))
WLA1=1.5/(FP1(U,L,.5)*CORR(FP1(U,L,.5)))
DO 50 CONTINUE
DO 205 K=1,118
WLS(1,K)=WLA(K)
WLS(2,K)=EM(K)
205 CONTINUE
CALL SORTR(WLS,-118,2)
DO 206 K=1,118
WLA(K)=WLS(1,K)
EM(K)=WLS(2,K)
206 CONTINUE
IBEG=WLA(1)-SPSW
IF (IBEG.LT.5400) IBEG=5400
IEND=WLA(118)+2.0*SPSW
IC=IEND-IBEG
IF (IC.GT.2000) GO TO 398
IWL=0
DO 300 IW=IBEG,IEND
IW=IW+1
LA(IWL)=IW
WL=IW
SUMA(IWL)=0.
DO 120 K=1,118
TT=(WT-WLA(K))/SPSW
IF (TT.GE.-1.0.AND.TT.LE.0.0) GO TO 191
IF (TT.GE.0.0.AND.TT.LE.1.0) GO TO 192
IF (TT.GE.1.0) GO TC 193
GO TC 120
191 TT=TT+1.
TT=TT*TI
1191 SUMA(IWL)=SUMA(IWL)+SPEC1(TT)*EM(K)
GO TC 120
192 TT=TT+1.
TT=TT*TI
1192 SUMA(IWL)=SUMA(IWL)+SPEC2(TT)*EM(K)
GO TC 120
193 TT=TT+1.
TT=TT*TI
1193 SUMA(IWL)=SUMA(IWL)+SPEC3(TT)*EM(K)
120 CONTINUE
300 CONTINUE
PRINT 6
6 FORMAT (///)
CALL PROB(TRAN,TPROB,M)
PRINT 71,U,L,TPROB
71 FORMAT(2X,2I3,E12.5)
IBGN=LA(1)-5399
IFIN=IBGN+IC
IF (IFIN.GT.3000) IFIN=3000
JA=10-U
KA=0
DO 910 I=IBGN,IFIN
KA=KA+1
A(I,JA)=SUMA(KA)*TPROB
910 CONTINUE
GO TC 10
398 PRINT 399,U,L,IC
397 FORMAT(2X,*V$=I3,3X,*V$$=I3* ARRAY REQUIRES DIMENSION*I5)
GO TC 10
400 CONTINUE
DO 402 I=1,3000
DO 401 JA=1,6
ZSUM(I)=ZSUM(I)+A(I,JA)
401 CONTINUE
402 CONTINUE
PRINT 930,(I,W,(A(IW-5399,JA),JA=1,6),ZSUM(IW-5399),IW=5400,8399)
930 FORMAT(2X,16,6E12.3,5X,E12.3)
WRITE(1)((A(I,JA),I=1,3000),JA=1,6)
END FILE 1
END
SUBCUTINE PROB(TRAN, TPROB, M)
DIMENSION TT(12,2)
IF (M .NE. 1) GO TO 5
READ 1, ((TT(I, J), J=1, 2), I=1, 12)
1 FORMAT(6(F3.0, E10.3))
PRINT 2, ((TT(I, J), J=1, 2), I=1, 12)
2 FORMAT(2X, F3.0, E10.3)
M=2
RETURN
5 DO 6 I=1, 12
6 CONTINUE
IF (TRAN .EQ. TT(I, 1)) GO TO 7
CONTINUE
GO TO 8
7 TPRCB=(TT(I, 2))**2
CONTINUE
RETURN
END
I-B PROGRAM SPECFIT

This program fits the computed synthetic band shapes to an observed spectrum to calculate a set of vibrational populations. The heart of the program is a package LSQVMT\(^2\) (not listed except for subroutine FCN) which is a non-linear least squares procedure using a method called variable metric minimization to determine the local minimum of a differentiable function. Subroutine TABLE defines the function and its derivative. Subroutine XANDY is a data handling routine which prepares the observed spectrum and the calculated band shapes for further processing. Subroutine GRAPH makes use of the LBL CALCOMP\(^3\) package to plot the observed and fitted spectra. Subroutine FCN is listed because it is modified from its form in the ISQVMT package.

\(^3\)CALCOMP package, LBL identification J5 BKY CC66, written by Bill Benson (Dec. 1965).
PROGRAM SPECFIT(INPUT,OUTPUT,TAPE2=INPUT,TAPE3=OUTPUT,TAPE1,TAPE98
1,TAPE99,TAPE4)
CALL LSGWMT
CONTINUE
CALL CCEND
END

SUBROUTINE FCN(N,DER,CHISQ,X,M1)
COMM/TITLE/CHAR(12)
COMM/ICH=EC/IGRAPH,ISTRT
DIMENSION DER(20),GRAD(20),WEIGHT(3000),YCALC(3000),X(20)
COMM/XY/SPEC(300C),XDATA(6,3000),NUMDTA
DIMENSION YDATA(3000)
M1=M1
IF (M1 .NE. 1) GO TO 400
READ (2,5) N,INVAR,ISTR,IFACR,IGRAPH
5 FORMAT (8110)
7 FORMAT (35HTHE NUMBER OF FITTING PARAMETERS =,14/38H THE NUMBER 0
*F INDEPENDENT VARIABLES =,14/28H THE NUMBER 0
485 DATA POINTS =,16)
READ(2,6)(CHAR(I),I=1,7)
6 FORMAT(7A10)  
WRITE(3,8)ICHAR(I),I=1,7)  
8 FORMAT(12HODATA POINTS)
WRITE (3,205)
205 FORMAT(11(X,E11.5))
CALL TABLE(FUNCT,GRAD,X,XDATA,M1)
RETURN
40C CHISQ=0.0
DO 410 I=1,N
DER(I)=0.0
410 CONTINUE
IF (M1 .NE. 2) GO TO 500
42C DO 450 I=1,NUMDTA
CALL TABLE(FUNCT,GRAD,X,XDATA(I,1),M1)
M1=2
CHISQ=CHISQ+WEIGHT(I)*((FUNCT-YDATA(I))**2)
DO 430 J=1,N
DER(J)=DER(J)+WEIGHT(I)*((FUNCT-YDATA(I))**2)*GRADT(J)
430 CONTINUE
450 CONTINUE
GO TO 600
500 CONTINUE
DO 510 I=1,NUMDTA
CALL TABLE (YCALC(I),GRADT,X,XCATA(I,I),M1)
M1=2
DIFFER=YCALC(I)-YDATA(I)
CHISQ=CHISQ+WEIGHT(I)*DIFFER**2
DO 520 J=1,N
DER(J)=DER(J)+WEIGHT(I)*DIFFER*2.0*GRADT(J)
520 CONTINUE
510 CONTINUE
IF (DIFFER.EQ.0) GO TO 600
IF (DIFFER.NE.0)
WRITE (3,525)
525 FORMAT (79H-INDEPENDENT VARIABLES--WEIGHT--DATA VALUE--CALCULATED VALUE--DIFFERENCE--RATIO)
DO 550 I=1,10
DIFFER=YCALC(I)-YDATA(I)
RATIO=DIFFER/YCALC(I)
IF (DIFFER.NE.0)
WRITE (3,530) (XDATA(J,I),J=1,6),YDATA(I),YCALC(I),DIFFER,RATIO
530 FORMAT(10(E12.5))
550 CONTINUE
600 CONTINUE
IF (M11.NE.4) GO TO 610
DO 605 I=1,NUMDTA
YCALC(I)=YCALC(I)/SPEC(I)
605 CONTINUE
IFLAG=2
IF (IGRAPH.EQ.1) CALL GRAPH(YCALC,IBGN,NUMDTA,IFLAG)
610 CONTINUE
RETURN
END

SUBROUTINE XANDY
COMMON/XY/SPEC(3000),XDATA(6,3000),NUMDTA
COMMON/ICHEC/IGRAPH,ISTRT
COMMON/YAMP/YM
DIMENSION EX(200)
DIMENSION CORR(3500)
LARGE AA(6,3000),A(3000,6)
READ 1,IBGN,ISTRT
1 FORMAT(215)
C*****IBGN IS WAVELENGTH OF START OF SPECTRA
C*****ISTRT IS WAVELENGTH OF FIRST CALCULATED CONTRIBUTION TO SPECTRA
READ 4,YM
4 FORMAT(EL0,0).
READ 11,NUMDTA
11 FORMAT(15)
NEX=NUMDTA-3000
IF (NUMDTA.GT.3000) NUMDTA=3000
READ 2,(SPEC(I),I=1,NUMDTA)
IF (NEX.GT.0) READ 2,(EX(I),I=1,NEX)
2 FORMAT(108,1)
READ(4)(CORR(I),I=1,3500)
IF (ENDFILE 4) 17,17
17 CONTINUE
READ(11)(A(I,J),I=1,3000),J=1,6)
IF (ENDFILE 1) 10,10
10 DO 5 I=1,3000
SPEC(I)=SPEC(I)/CORR(I+IYBGN-5000)
DO 3 J=1,6
AA(J,I)=A(I,J)/CORR(I+IYBGN-5000)
3 CONTINUE
5 CONTINUE
IC=1YSTRT-5400
ID=IYBGN-5400
IB=IC-ID
IF (IB) 115,12,12
12 NUMDTA=NUMDTA-IC
DO 7 I=1,6
DO 6 J=1,NUMDTA
XDATA(J,I)=AA(J,IC+I)
6 CONTINUE
7 CONTINUE
DO 8 I=1,NUMDTA
SPEC(I)=SPEC(I+IB)
8 CONTINUE
GO TO 15
15 DO 14 J=1,6
DO 13 I=1,NUMDTA
13 CONTINUE
14 CONTINUE
15 CONTINUE
DO 20 I=1,NUMDTA
IF (SPEC(I).LE.1.0) SPEC(I)=(SPEC(I-1)+SPEC(I+1))/2.
20 CONTINUE
IFLAG=1.
IF (IGRAPH.EQ.1) CALL GRAPH(SPEC,IYBGN,NUMDTA,IFLAG)
DO 21 I=1,NUMDTA
SPEC(I)=1./SPEC(I)
DO 22 J=1,6
XDATA(J,I)=XDATA(J,I)*SPEC(I)
22 CONTINUE
21 CONTINUE
RETURN
END
SUBROUTINE TABLE(F,G,X,T,M1)
DIMENSION G(9),X(9),T(9)
IF (M1.EQ.1) RETURN
F=0,
DO 1 I=1,6
X(I)=AUS(X(I))
F=F+T(I)*X(I)
G(I)=T(I)
1 CONTINUE
RETURN
END

SUBROUTINE GRAPH(Y,IBGN,N,IFLAG)
COMMON/CPPOOL/XMIN,XMAX,YMIN,YMAX,CXMIN,CXMAX,CYMIN,CYMAX
COMMON/YAMP/YM
COMMON/ICHEC/IGRAPH,ISTRT
COMMON/TITLE/CHAR(12)
DIMENSION X(3100),Y(N)
CYMAX=680.,CXMAX=920.,YMIN=5400.,XMAX=8499.
YM=0.0
YMAX=YM
IF (IFLAG.EQ.2) GO TO 99
DO 1 I=1,N
X(I)=YSTRT+1-1
1 CONTINUE
CALL CCBGN
CALL CCGRID(1,31,5,6HNOBLBL,1,10)
CALL CCPLT(X,Y,N,6HNOJOIN,3,1)
RETURN
99 CONTINUE
CALL CCPLT(X,Y,N)
CALL CLLTR(200.,900.,0,2,CHAR,30)
CALL CCNEXT
IGRAPH=2
RETURN
END
I-C PROGRAM NEWHOP

This program reads the data of an intensity versus pressure experiment, sorts the points in order of increasing pressure, finds the best least squares fit of a 7th order polynomial to the data, plots the data and the polynomial function, and punches values of the intensity at convenient pressure intervals.

The driver program, NEW, reads data, subtracts background, and interprets pressure data in terms of microns. Subroutine GRAPH utilizes the CALCOMP package. Subroutine OHFIT defines the polynomial function for which the LSQPOL$^4$ (not listed) finds the coefficients. Subroutine PNCHR writes calculated values of the function on a file for punching and subroutine SORT$^5$ (not listed) sorts the experimental data in order of increasing pressure.

$^4$Subroutine LSQPOL, LBL identification E2 AN E206; written by B. S. Garbow, Argonne National Laboratory; modified by B. Dempster, LBL, (May 1959).

PROGRAM NEW(INPUT,OUTPUT,TAPE1,TAPE98,TAPE99)

DIMENSION ZI(I(20)),ZI0(I(20)),ZP(I(200)),ZI(20C),ZP8(20),ZI8(20),ZIC(20)

1)

DIMENSION XCURR(19),NPEAK(19),SCALE(19)

COMMON/NNAME/TITLE(2)

COMMON/KOUNT,NPRES,PRES(25)

DIMENSION PI0(20),XI0(20)

INTEGER DIM1,DIM2,DIM3

DATA TITLE(1)/'HOMSPECTRAL P/

READ 5,(XCORR(I),I=1,19)

5 FORMAT(13F6.2)

KOUNT=0

READ 1,NEXP,DIM1,DIM2,DIM3

1 FORMAT(4I5)

READ 6,(NPEAK(I),I=1,NEXP)

6 FORMAT(20I3)

READ 1,NPRES

READ 7,(SCALE(I),I=1,NEXP)

7 FORMAT(IOF8.5)

READ 3,(ZIC(I),I=1,NEXP)

READ 3,(PI0(I),XI0(I),I=1,NEXP)

READ 101,(PRES(I),I=1,NPRES)

DIM2=DIM2+1

2 KOUNT=KOUNT+1

IF (KOUNT,GT,NEXP) GO TO 100G

IF (KOUNT,GT,2) DIM2=61

READ 3,(ZPI(I),ZI0(I),I=1,DIM1)

READ 3,(ZPI(I),ZI(I),I=1,DIM2)

READ 2,(ZP8(I),ZI8(I),I=1,DIM3)

3 FORMAT(10F8.5)

IF (KOUNT,GT,1) GO TO 2

ZPI(I)=PI0(KOUNT)

ZI(I)=XI0(KOUNT)

C *** CARD FOR 100 MICRON SCALE *****

ZI0(I)=ZI0(I)/50.

ZI(I)=ZI(I)-ZIC(KOUNT)

4 CONTINUE

K=NPEAK(KOUNT)

ENCODE(6,10,TITLE(2))

10 FORMAT(4HEAK,12)

DO 8 I=1,DIM2

8 CONTINUE

C *** ROUTINE TO SKIP FIRST 15 POINTS *****

DIM2=DIM2-15

DO 11 I=1,DIM2

ZPI(I)=ZPI(I+15)

ZI(I)=ZI(I+15)

11 CONTINUE

CALL GRAPH(ZPI,ZI,DIM2,8,MPRESSURE,9HINTENSITY)

CALL (HFIT(ZPI,ZI,DIM2)

DIM2=DIM2+15

GO TO 2

1000 CONTINUE

END FILE 1
SUBROUTINE GRAPH(X,Y,N,RX,RY)
COMMON/NAME/TITLE(2)
COMMON/CCP00L/XMIN,XMAX,YMIN,YMAX,CCXMIN,CCXMAX,CCYMIN,CCYMAX
DIMENSION ROUND(4),X(1),Y(1)
COMMON/POINT/PLACE
INTEGER PLACE
DATA (ROUND(I),I=1,4)/1.,1.,2.,2.5,5./
DATA NROUND,PART/4,10./
IF(PLACE.EQ.1) GO TO 1
CALL CCPGN
CALL LINEUP(X,N,ROUND,NROUND,PART,XMIN,XMAX)
CALL LINEUP(Y,N,ROUND,NROUND,PART,YMIN,YMAX)
CALL CGGRID(1,10,10,6,0,LABELS,1,10,10)
CALL CLPLOT(X,Y,N,6,NOJOIN,8,1)
CALL CCLTK(350.,10.,0.,1.,RX)
CALL CCLTR(10.,350.,1.,1.,RY)
CALL CCLTK(200.,900.,0.,2.,TITLE,16)
RETURN
1 CONTINUE
CALL CCPLOT(X,Y,N)
PLACE = 0
CALL CCGNEXT
RETURN
END

SUBROUTINE OHFIT(X,Y,N)
DIMENSION X(200),Y(200),1(200),SUM(1),A(20,8),B(20,1),C(20 10,8),W(200)
DIMENSION YCALC(200)
INTEGER PLACE
COMMON/POINT/PLACE
L=1
PLACE=1
M=8
DO 1 I=1,N
W(I)=1.0
1 CONTINUE
CALL LSQPOL(X,Y,W,RESID,N,SUM,L,A,B,M)
PRINT 2,(B(I,1),I=1,M)
2 FORMAT(//5X,8E13.5)
PRINT 3,SUM
3 FORMAT(10X,E13.5)
CALL SORT(N,X)
DO 4 I=1,N
YCALC(I)=B(1,1)+B(2,1)*X(I)+B(3,1)*X(I)**2+B(4,1)*X(I)**3+B(5,1)*X(I)**4+B(6,1)*X(I)**5+B(7,1)*X(I)**6+B(8,1)*X(I)**7
4 CONTINUE
CALL GRAPH(X,YCALC,N,R1,R2)
CALL PNCHR(B)
RETURN
END

SUBROUTINE PNCHR(C)
DIMENSION C(ZC,1),Y(100)_
COMMON/COIN/NPRES,PRES(25)
DO 1 I=1,NPRES
Y(I)=C(1,1)+C(2,1)*PRES(I)+C(3,1)*PRES(I)**2+C(4,1)*PRES(I)**3+C(5
+1)*PRES(I)**4+C(6,1)*PRES(I)**5+C(7,1)*PRES(I)**6+C(8,1)*PRES(I)
**7
1 CONTINUE
WRITE(1,2)(Y(I),I=1,NPRES)
2 FORMAT(10F8.1)
RETURN
END
I-D PROGRAM QUTERN

This program does a least squares minimization of a kinetic model to determine the best values of desired rate constants. This program makes use of the MINUIT$^6$ package of programs for minimization of a function of n variables. This package contains Monte Carlo, simplex, and variable matrix minimization procedures plus various error analysis routines.

Subroutine SETUP is an initializing routine for reading data and printing desired input tables.

Control of the MINUIT package is accomplished by a series of COMMAND cards (described in the writeup) which specify minimization parameters and call the desired routines.

\footnote{MINUIT package, written by F. James and M. Roos, CERN, (October, 1971). Adapted for use on LBL 7600 by D. Austin.}
PROGRAM QUERNR(INPUT,OUTPUT,PUNCH,TAPE1=INPUT,TAPE2=OUTPUT,TAPE3=
  PUNCH)
COMMON/HEAD/INFO(8)
COMMON/NX/NUMDTA
READ 1,INFO(I),I=1,3
1 FORMAT(8A10)
READ 5,NUMDTA
5 FORMAT(I5)
CALL SETUP
CALL MINNEW
END

SUBROUTINE FCN(NPAR,G,F,X,IFLAG)
DIMENSION X(6),G(6)
COMMON/NX/NUMDTA
COMMON/SURF/TAU(10,10)
DIMENSION RK2(10),RK3(10)
DATA RK3/2.5E-12,3.2E-12,4.2E-12,5.4E-12,6.9E-12,8.9E-12,1.1E-11,1
  4.E-11,1.8E-11,2.3E-11/
C *** MY VALUES ****
DATA RK2/0.0,0.0,0.0,0.0,3.7E-12,4.5E-12,7.2E-12,8.5E-12,8.9E-12,
1.1E-11/
COMMON/SURF/TAU(10,10),TAUVV(10,10),CO3,CM,CMP(50)
INTEGER V
IF (IFLAG.NE.1) GO TO 10
READ 3,FVH
3 FORMAT(F8.4)
READ 4,V
4 FORMAT(I5)
RETURN
10 CONTINUE
F=O.O
DO 5 I=1,NPAK
G(I)=O.O
5 CONTINUE
DO 10 ICALL=1,NUMDTA
FD(1)=O.O
DO 10 I=1,10
FD(4)=FD(4)+RK3(I)*COH(ICALL,I)
10 CONTINUE
FD(1)=O.O
IF (V.EQ.9) GO TO 13
IV=V+1
DO 12 I=1,IV
FD(3)=FD(3)+TAUVV(I,V)*COH(ICALL,I+1)
12 CONTINUE
13 CONTINUE
P=O.O
IF (V.LT.9) P=POH1=COH(ICALL,V+2)
FN1=(2.6E-11)*CO3
FN2=F2
FN3=CMP(ICALL)*POH1
FD1=TAUVVV
FD2=CMP(ICALL)
FD3=RK2(V+1)*CO3
FD5=0.2
FD6=1.0/SQRT(CMP(ICALL))
FN=X(1)*FN1+FN2*X(2)*FN3
FD=FD1+X(3)*FD2+FD3*X(4)*FD4+FD5*X(5)*FD6
FCHEC=FN/FD
IF(IFLAG.EQ.3) PRINT 131,FN1,FN2,FN3,FD1,FD2,FD3,FD4,FD6,FCHEC
131 FORMAT(X,10E12.5)
FUNC=(FN/FD-COH(ICALL,V+1))
F=F+FUNC**2
IF(IFLAG.NE.3) GO TO 200
G(1)=G(1)+2*FUNC*FN1/FD
G(2)=G(2)+2*FUNC*FN3/FD
G(3)=G(3)+2*FUNC*FD2*FM/FU**2
G(4)=G(4)+2*FUNC*FD4*FM/FU**2
G(5)=G(5)+2*FUNC*FD6*FM/FU**2
200 CONTINUE
100 CONTINUE
RETURN
END

SUBROUTINE SETUP
COMMON/NX/NUMDATA
COMMON/DATA/COH(50,10)
COMMON/SLICE/TAUV(10),TAUVV(10,10),CO3,CM,CMP(50)
COMMON/HEAD/INFO(8)
1 FORMAT(1CF8.4)
READ 1,((TAUV(I,J),J=1,10),I=1,10)
READ 3,((TAUVV(I,J),J=1,10),I=1,10)
READ 2,(CMPP(I),I=1,NUMDATA)
READ 3,CO3,CM
DO 6 J=1,10
READ 3,((COH(I,J),I=1,10),NUMDATA)
6 CONTINUE
3 FORMAT(8E10.6)
PRINT 2
2 FORMAT(1H1,5X,*I*8X4 *15X*OH(4)*12X*OH(5)*12X*OH(6)*12X*OH(7)*12X
*OH(8)*12X*OH(9)*)
PRINT 4,((CMPP(I),J=1,10),I=1,NUMDATA)
4 FORMAT(3X,15,7(5X,E12.5))
PRINT 5,CO3,CM
5 FORMAT(//5X,*O3=*E12.5*BACKGROUND (M)=*E12.5)
PRINT 10,((INFO(I),I=1,9)
10 FORMAT(3X,8A10)
RETURN
END
APPENDIX II.

Error Analysis

Analysis of the magnitude of error in this system is very difficult due to the complexity of the procedure required to obtain a rate constant. Random errors due to the experimental apparatus and data gathering are judged to be within the statistical errors calculated over an entire series of experiments. Systematic errors were dealt with by frequently recalibrating wavelength and pressure measuring apparatus. Only relative spectral intensity measurements were required in calculations and no calculations were made with data which would not contain true relative significance; i.e. experiments done on separate days or even an experiment interrupted for more than a few minutes.

The chemiluminescence quenching technique, though invaluable for observing a multistate system, has the uncertainty of relying on assumed radiative lifetimes to put absolute values on rate constants. The radiative lifetime of at least one band must be known and the lifetimes of other bands may be computed from relative transition probabilities. Some uncertainty exists here, too, because calculated transition probabilities vary depending upon assumptions, most notably the form of expansion for the dipole moment. Fortunately all calculations agree quite well for the high overtone bands which were observed in this work. In a multistate system in which the states are coupled by stepladder quenching, errors in determining quenching rate constants accumulate with each lower state. However the ability of the assumed kinetic model to fit the data with only two parameters is compelling
evidence for the validity of the results.

Two measures of statistical significance may be made on the results of an individual experiment. These are the standard deviation of a parameter as derived from the diagonal elements of the covariance matrix and the correlation coefficients between parameters derived from the off-diagonal elements of the covariance matrix. In all cases the standard deviation of a parameter was of the order of hundredths of a percent. This is understandable because the calculation proceeded until a minimum was found and the standard deviation of parameter values which satisfied that minimum was very small.

Of more interest were the correlation coefficient between parameters. These can be used to test the assumptions that hydroxyl-hydroxyl reactions and wall quenching were fairly insignificant terms in the calculation. For vibrational level nine of a typical experiment, correlation coefficients (ρ) were as follows:

\[
|\rho_{31}| = 0.73 \quad |\rho_{34}| = 0.07 \quad |\rho_{35}| = 0.00
\]

where ρ_{31} is the correlation between parameters x(3) and x(1). Parameter x(1) involved the rate of reaction into a vibrational level and hydrogen atom concentration, parameter x(3) was the quenching rate constant, parameter x(4) measured hydroxyl-hydroxyl reaction, and parameter x(5) was the wall quenching coefficient. We see there is high correlation between the rate constant and x(1) and little or no correlation between the rate constant and x(4) or x(5). This fully supports the assumptions just mentioned. For the same experiment and vibrational level four,
$|\rho_{31}| = 0.30$ and other correlations are correspondingly smaller. This is expected and is due to the accumulation of errors and the resulting loss of functional dependence on the parameters.

The time honored method for reducing error and gaining statistical significance is to increase the sample size, assuming systematic errors are fully accounted for. If the sample size is greater than one, the arithmetic mean is then usually chosen as the preferred value. It is then necessary to make some estimate of error, not of an individual measurement, but of the mean value. This may be done by computing the standard deviation of the mean which is defined as follows,

$$\sigma_{\bar{x}} = \frac{\sigma}{\sqrt{n}}$$

where $\sigma_{\bar{x}}$ is the standard deviation of a single measurement and $n$ is the number of measurements. The standard deviation of the mean, expressed as percentage, for the rate constants determined in this work is presented in Table A. Results for argon are not included because only one complete experiment was done, and the results for oxygen and deuterium are identical to the mean deviation because only two complete experiments were done for each.

It is evident from Table A that statistical error limits have little meaning for this work because of the unknown errors accompanying radiative lifetimes and transition probabilities. It would be more meaningful to judge from experimental scatter that error limits for the ozone rate constants should be about $\pm 20\%$ and for the quenching rate constants to increase from $\pm 20\%$ at $v=9$ to $\pm 50\%$ at $v=4$. 
Table A. Mean Deviation Error Limits for Rate Constants (percentage)

<table>
<thead>
<tr>
<th>Reactant</th>
<th>9</th>
<th>8</th>
<th>7</th>
<th>6</th>
<th>5</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₃</td>
<td>±2.9</td>
<td>±1.7</td>
<td>±1.6</td>
<td>±1.8</td>
<td>±2.0</td>
<td>±1.9</td>
</tr>
<tr>
<td>H₂</td>
<td>±5.2</td>
<td>±23.0</td>
<td>±18.8</td>
<td>±17.1</td>
<td>±10.3</td>
<td>±15.0</td>
</tr>
<tr>
<td>N₂</td>
<td>±13.0</td>
<td>±7.6</td>
<td>±12.9</td>
<td>±14.4</td>
<td>±19.0</td>
<td>±28.2</td>
</tr>
<tr>
<td>O₂</td>
<td>±2.9</td>
<td>±8.3</td>
<td>±1.3</td>
<td>±7.5</td>
<td>±7.8</td>
<td>±3.6</td>
</tr>
<tr>
<td>D₂</td>
<td>±1.0</td>
<td>±1.6</td>
<td>±13.6</td>
<td>±4.1</td>
<td>±9.3</td>
<td>±15.0</td>
</tr>
</tbody>
</table>
APPENDIX III.

Models for Hydroxyl Radicals in the Stratosphere

There is currently a great deal of interest in determining and understanding the chemistry of the stratosphere as Man now has the capability of severely perturbing its natural state. The ozone layer in the stratosphere is vital to life on this planet, so it is very important to understand the individual processes which create or destroy ozone, and which taken together are responsible for maintaining the natural steady state.

Chemical destruction of ozone by the HO$_x$ system; the set of free radicals H, HO, HOO; is one of several different removal processes which balances the production of ozone. This system is responsible for about 10 to 20% of the total ozone destruction, which puts it on a par with the O$_x$ system, an order of magnitude faster than transport processes, and 3 to 6 times slower than the NO$_x$ system. However the chemistry of the HO$_x$ system has always been written in terms of ground state hydroxyl even though it is known that the reaction of hydrogen atoms with ozone produces vibrationally excited hydroxyls. The significance of excited hydroxyls in the chemistry of the stratosphere has not been explored.

Because of the exceeding complexity of the chemistry of the stratosphere, the models studied here include only chemistry of the O$_x$ and HO$_x$ systems. Further, because of the great uncertainties in rate constants for reaction of excited species, the results of these
calculations must be considered relative and only very roughly as a true measure of the stratosphere. The results may be used for judging the relative importance of each excited hydroxyl model, or the relative importance of one reaction compared to another within a model.

The computation was done with a chemical kinetics package authored by Whitten and modified by Whitten to be applicable to the stratosphere. The modifications include calculating the complete solar spectrum for any time of the day, for any elevation at any specified latitude. Time of day and elevation may also be varied within the program so a day long picture of the chemistry at all elevations may be obtained.

Three models for hydroxyl radicals in the stratosphere were used in the calculations. These models are as follows.

1) Ground State Model

In this model all reactions which produce hydroxyl radicals are assumed to produce only ground state hydroxyl radicals. The total set of reactions considered is listed below.

\[ \text{O}_2 + h\nu \rightarrow 20^3P \]  \hspace{1cm} (1)
\[ \text{O}_3 + h\nu \rightarrow \text{O}_2 + 0(^1D) \]  \hspace{1cm} (2)
\[ \text{O}_3 + h\nu \rightarrow \text{O}_2 + 0(^3P) \]  \hspace{1cm} (3)
\[ \text{H}_2\text{O} + h\nu \rightarrow \text{H} + \text{HO} \]  \hspace{1cm} (4)
\[ 0(^1D) + M \rightarrow 0(^3P) + M \]  \hspace{1cm} (5)
\[ 0(^1D) + \text{O}_3 \rightarrow \text{O}_2 + 20(^3P) \]  \hspace{1cm} (6)
\[ 0(^1D) + \text{H}_2\text{O} \rightarrow 2\text{HO} \]  \hspace{1cm} (7)
\[ 0(^3P) + \text{O}_2 + M \rightarrow \text{O}_3 + M \]  \hspace{1cm} (8)
\[ 0(^3P) + \text{O}_3 \rightarrow 2\text{O}_2 \]  \hspace{1cm} (9)
Rate constants were obtained from references 40 and 94. Photolysis rates were calculated by the program with absorption cross sections from the literature written into the program. Rates for reactions (14) and (17) were set to zero for this model. Reaction (20) actually produces \( \text{H}_2\text{O}_2 \), but it is assumed that this is instantly photolyzed to produce two hydroxyls.

2) Intermediate Excited Hydroxyl Model

In this model the same basic reaction scheme is used, except that reaction (13) is now allowed to produce excited hydroxyl radicals. The rate constant for reaction (13), \( 2.6 \times 10^{-11} \text{ cm}^3/\text{molec-sec} \), is partitioned to produce excited hydroxyls in vibrational levels four through nine. Reaction (14) is allowed to occur for vibrational levels three through nine and reaction (15) is assumed for vibrational levels zero through two. Reaction (17), quenching, is allowed to
proceed with rate constants for each level being 80% of the value for quenching with \(\text{N}_2\) and 20% of the value for quenching with \(\text{O}_2\). Rate constants for all other species reacting with excited hydroxyl were estimated by assuming the rate constant for reaction with \(\text{HO}(v=9)\) was an order of magnitude greater than for reaction with \(\text{HO}(v=0)\) and then scaling the intermediate values appropriately. Where an order of magnitude increase made the reaction unrealistically fast as in the case of \(\text{HO} + \text{HOO}\), the rate constant for \(\text{HO}(v=9)\) was made only 2.5 times larger.

3) Maximum Excited Hydroxyl Model

In this model, other reactions which produce hydroxyl radicals are assumed to produce hydroxyl radicals which are vibrationally excited as high as energetically possible. The following reactions were substituted for the similarly numbered ones in the first model.

\[
\begin{align*}
\text{O}^{1}\text{D} + \text{H}_2\text{O} & \rightarrow \text{HO}(v=0) + \text{HO}(v=4) \\
\text{O}^{3}\text{P} + \text{HO} & \rightarrow \text{HO}(v=6) + \text{O}_2 \\
\text{O}_3 + \text{HO} & \rightarrow \text{HO}(v=3) + 2\text{O}_2 \\
\text{HOO} + \text{HOO} & \rightarrow 2\text{HO}(v=8) + \text{O}_2
\end{align*}
\]

Reaction (20a) is written assuming instantaneous photolysis of \(\text{H}_2\text{O}_2\) with a photon of wavelength 205 nm.

As a basis for comparison with the excited hydroxyl models, it is necessary to show results for model 1 calculations. All calculations were done with the sun at midday in early summer at 45° N latitude.
As mentioned earlier, concentrations for various species are merely the results of model calculations, yet they are of the order of magnitude of the real stratosphere, so some feeling may be gained for the important processes occurring in the stratosphere. We first look at the hydroxyl concentration versus elevation.

<table>
<thead>
<tr>
<th>Elevation (km)</th>
<th>28</th>
<th>33</th>
<th>38</th>
<th>43</th>
<th>48</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(_2)O (molecules/cm(^3))</td>
<td>2.1(6)</td>
<td>3.7(6)</td>
<td>7.7(6)</td>
<td>1.0(7)</td>
<td>7.2(6)</td>
</tr>
<tr>
<td>(2.1(6) = 2.1 \times 10^6)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

These concentrations may be compared to \(O_3\): 1.2(11), \(O(3P)\): 8.1(9), \(O(1D)\): 5.3(2) all at 48 kilometers. Another result of interest is the instantaneous rate of reaction for those reactions involving hydroxyl radicals. Some of these may be seen in Table B. Looking at the rates at 48 km., we see that the primary formation and destruction of H\(_2\)O occurs through the reactions with \(O(3P)\). Reactions involving ozone are secondary. Since reactions which destroy ozone are of interest, the following comparison is made.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Instantaneous rate at 48 km</th>
</tr>
</thead>
<tbody>
<tr>
<td>(O_3 + H)O</td>
<td>3.6(4) molecules/cm(^3)-sec</td>
</tr>
<tr>
<td>(O_3 + H)</td>
<td>6.2(5) &quot;</td>
</tr>
<tr>
<td>(O_3 + HOO)</td>
<td>2.2(3) &quot;</td>
</tr>
<tr>
<td>(O_3 + O(3P))</td>
<td>3.9(6) &quot;</td>
</tr>
<tr>
<td>(O_3 + h\nu)</td>
<td>8.9(8) &quot;</td>
</tr>
</tbody>
</table>
Table B. Instantaneous Rates of Hydroxyl Radical Reactions in the Stratosphere (molecules/cm$^3$-sec)

<table>
<thead>
<tr>
<th>Elevation (km)</th>
<th>Formation Reactions</th>
<th>Destruction Reactions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>7</td>
<td>11</td>
</tr>
<tr>
<td>28</td>
<td>2.6(4)</td>
<td>2.3(4)</td>
</tr>
<tr>
<td>33</td>
<td>4.2(4)</td>
<td>1.1(5)</td>
</tr>
<tr>
<td>38</td>
<td>6.4(4)</td>
<td>5.4(5)</td>
</tr>
<tr>
<td>43</td>
<td>6.1(4)</td>
<td>1.7(6)</td>
</tr>
<tr>
<td>48</td>
<td>2.5(4)</td>
<td>1.9(6)</td>
</tr>
</tbody>
</table>

Reactions

1. $O(^1D) + H_2O \rightarrow 2HO$
2. $O(^3P) + HOO \rightarrow HO + O_2$
3. $O_3 + H \rightarrow HO + O_2$
4. $O_3 + HOO \rightarrow HO + 2O_2$
5. $HOO + HOO \rightarrow 2HO + O_2$
6. $O(^3P) + HO \rightarrow O_2 + H$
7. $O_3 + HO \rightarrow HOO + O_2$
8. $HO + HOO \rightarrow H_2O + O_2$
It is obvious that in the daytime destruction of ozone by the \( \text{HO}_x \) system is small.

The results for the other two models will be examined only at 48 km. because the highest concentrations of excited hydroxyl radicals are found there and any effect would be most pronounced there. For model 2, the following concentrations are found.

<table>
<thead>
<tr>
<th>( v )</th>
<th>9</th>
<th>7</th>
<th>5</th>
<th>3</th>
<th>1</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{HO} ) (molecules/cm(^3))</td>
<td>1.9(1)</td>
<td>3.0(1)</td>
<td>9.5(1)</td>
<td>5.7(2)</td>
<td>3.2(3)</td>
<td>7.2(6)</td>
</tr>
</tbody>
</table>

It is seen that steady state concentrations of excited hydroxyls are very low. The reason is found in the following instantaneous rates which occur at 48 km.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Instantaneous rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{HO}(v=9) + \text{O}^3) ( \text{P} ) ( \text{O}_3 ) ( \text{M} ) ( \text{HO}(v=1) + \text{O}^3) ( \text{P} ) ( \text{HO}(v=1) + \text{O}_3 ) ( \text{HO}(v=1) + \text{M} ) ( ) ( ) ( ) ( ) ( ) ( )</td>
<td></td>
</tr>
<tr>
<td>6.1(1) molecules/cm(^3)-sec ( ) ( ) ( ) ( )</td>
<td></td>
</tr>
<tr>
<td>2.6(1) ( ) ( )</td>
<td></td>
</tr>
<tr>
<td>2.2(5) ( ) ( )</td>
<td></td>
</tr>
<tr>
<td>1.3(3) ( ) ( )</td>
<td></td>
</tr>
<tr>
<td>4.0(2) ( ) ( )</td>
<td></td>
</tr>
<tr>
<td>6.2(5) ( ) ( )</td>
<td></td>
</tr>
</tbody>
</table>

Quenching proceeds several orders of magnitude faster than any other process and severely limits the steady state population of excited hydroxyl radicals. For this model, the sum of rates for hydroxyl reacting with ozone is 3.4% faster than the rate in model 1.

In the maximum excited hydroxyl model, the following concentrations are calculated.
The concentrations of excited hydroxyls have increased considerably in the lower vibrational states due to reaction (11a), but are still small compared to ground state hydroxyl. In fact, with no direct chemical production of ground state hydroxyl, the concentration is the same as in the first two models. Again, the reason is extremely rapid quenching.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Instantaneous rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>HO(v=1) + O(^3)P</td>
<td>5.3(3) molecules/cm(^3)-sec</td>
</tr>
<tr>
<td>HO(v=1) + O(_3)</td>
<td>1.6(3)</td>
</tr>
<tr>
<td>HO(v=1) + M</td>
<td>2.5(6)</td>
</tr>
</tbody>
</table>

The sum of rates for hydroxyl reacting with ozone is 13% faster than for model 1, but this still has no effect on daytime chemistry.

In calculations done with each model for a 14 hour period from sunrise to sunset, the total ozone column in the stratosphere was unchanged in the two excited hydroxyl models.

Nighttime chemistry in the stratosphere is much slower since species like O\(^1\)D disappear within a few seconds of sunset. A major feature of nighttime chemistry is the buildup of certain species, for example H\(_2\)O\(_2\), which are very rapidly photolyzed at sunrise. However vibrationally excited hydroxyl radicals are still quenched efficiently and in no way alter the chemistry resulting from the non-excited HO\(_x\) species.
The nighttime airglow, which is a direct indication of the presence of excited hydroxyls at night, originates in the mesosphere at altitudes of 80-90 km. At that altitude excited hydroxyls would have a much longer lifetime and would be expected to be a significant factor in the chemistry of the mesosphere. However at the present, knowledge of the chemistry of the mesosphere and of rate constants for reaction of excited species is too scant to allow extension of this modelling process to that altitude.
REFERENCES


39. Handbook of Chemistry and Physics, 43rd ed. (Chemical Rubber Co., Cleveland, Ohio (1962)).
40. Climatic Impact Assessment Program, Mono #1 section 5.9 (1973).
85. S. D. Worley, private communication.
92. H. S. Johnston, "Photochemistry in the Stratosphere--with Applications to Supersonic Transports" LBL-2217 (Sept. 1973) and other references therein.


This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.