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G. E. Streit and H. S. Johnston

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Reactions and Quenching of
Vibrationally Excited Hydroxyl Radicals

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Abstract

Rate constants for the deactivation of vibrationally excited hydroxyl radicals by the inert gases Ar, O₂, N₂, H₂, and D₂ have been determined. Additionally the rate constants for the reaction HO(v) + O₃ → products have been measured and found to decrease from 11×10^{-12} to 3.7×10^{-12} cm³ molecule⁻¹ sec⁻¹ from v=9 to v=4. Hydroxyl radicals were generated in a large tank at low pressures from the reaction of hydrogen atoms and ozone. The radicals were formed in excited vibrational states (v ≤ 9), and the excited radicals, v=4 to 9, were observed by visible light emission from high overtone transitions. Vibrational populations and the rate constants for loss processes were deduced from observations over a wide range of wavelength and pressure fitted to comprehensive model of the system.

Introduction

It has been known since Meinel first observed hydroxyl emission bands in the night sky airglow² that the reaction

which is 77 kcal/mole exothermic produces hydroxyl radicals excited up through vibrational level nine of the $^2\Pi_1$ ground electronic state. The vibration-rotation emission spectrum of the hydroxyl system has since been studied many times, both by observation of the airglow³⁻⁵ and by observations in the laboratory⁶⁻⁹. In most of these studies, the intent was to measure or derive the initial vibrational population distribution produced by reaction (1). Coltharp and coworkers¹⁰ have reported rate constants for the reaction of vibrationally excited hydroxyl radicals with ozone:

and rate constants for vibrational energy transfer by inert molecules M:

They observed the time dependent decay, in a fast flow tube, of the $v=2$ 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.

In this work, the rate constants for the reaction of ozone and excited hydroxyl radicals have been re-investigated in a low pressure system by observing chemiluminescence emission from the $\Delta v=4,5$, and 6

overtone bands in the spectral region 5500Å - 8500Å. Because there is considerable overlap of the bands in the region, it was necessary to obtain vibrational populations 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 dependence of emission intensity on ozone concentration and by interpreting this behavior in terms of a comprehensive model of the system.

In a second series of experiments, the reactants were held constant, and vibrational quenching of excited hydroxyl radical (v from 4 to 9) was studied by addition of argon, nitrogen, oxygen, hydrogen, or deuterium. This study reveals the energy dependence of quenching interactions and, to a simple approximation, the nature of those interactions.

The rate constants obtained here, including those for quenching by nitrogen and oxygen, have been applied to a computer model of the stratosphere¹¹ to determine the effect, if any, that vibrationally excited hydroxyl radicals have in the stratosphere. Three versions of the chemical model were calculated. One allows for the production of ground state ($v=0$) hydroxyl radicals only, the second allows for the production of excited hydroxyl radicals by reaction (1) only, and the third allows for the production of excited hydroxyl radicals by every reaction possible.

Experimental

The system was a 340 liter stainless steel cell with multiple inlets for gas delivery and pressure measurement. The cell was fitted with two inch diameter quartz end windows for chemiluminescence

detection or for a single pass absorption measurement with a path length of 139 cm. The cell was pumped by a six inch oil diffusion pump and was protected by a chevron type water cooled baffle and a liquid nitrogen trap.

The detection system was a 0.3 meter McPherson scanning monochromator equipped with a 1200 line/mm grating blazed at $5000\text{\AA}$ and an EMI 9558QA photomultiplier tube with an S-20 type spectral response. A high gain amplifier/discriminator supplied by Solid State Radiation converted the signal to uniform pulses and the SSR Data Converter supplied either digital or analog signals proportional to the photon count rate. A spectrum could either be fed directly to a laboratory mini-computer or be punched on paper tape for processing on a CDC 7600 computer.

The purity and supplier of each gas used in this work is as follows: hydrogen, 99.999%, Matheson; oxygen, 99.6%, Lawrence Berkeley Laboratory; nitrogen, 99.999%, LBL; deuterium, 99.97%; Liquid Carbonic; argon, 99.999%, LBL. The oxygen used for ozone preparation was purified by passing it over 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_2O_5). Gases used for vibrational quenching experiments were taken directly from the cylinders.

Ozone was prepared by flowing purified oxygen through an electric discharge ozonizer and was separated from oxygen by trapping it on silica gel held at -78°C . Ozone could be stored for long periods of time in this trap without significant loss. Prior to an experiment, residual oxygen was removed

by pumping the trap to 0.5 Torr, well below the partial pressure of ozone at -78°C . During an experiment ozone flowed into the cell under its own pressure. Cook and coworkers¹² present a complete discussion of the separation of ozone from oxygen by adsorption on silica gel.

Ozone concentration in the cell was determined by measuring absorption at $2550\text{\AA}$. The source was a deuterium lamp and the absorption cross section at that wavelength was determined by Ackerman¹³ to be $1.119 \times 10^{-17} \text{ cm}^2$.

Hydrogen atoms were produced by flowing moistened hydrogen (2-3% water content) with a very small amount of added argon through a 13mm quartz discharge tube placed in a number five microwave discharge cavity¹⁴. The microwave power supply was a Burdick 2450 Mhz diathermy unit.

Before any set of experiments, the cell and all gas delivery lines were baked (250°C) and pumped for 3-5 days to about 5×10^{-6} Torr. During an experiment, the hydrogen flow through the discharge was typically 4.8 to 15×10^{17} molecules sec^{-1} . With the added argon needed to maintain the discharge, the resultant cell pressure was 4×10^{-4} Torr. Ozone was then added to set up an initial hydroxyl distribution at a total pressure of $0.8 - 1.0 \times 10^{-3}$ Torr. Pressure was measured during experiments by a Datametrics capacitance pressure transducer with a most sensitive range of one milli Torr full scale.

Data were gathered by two different methods. (1) The spectrum was scanned from $5500\text{\AA}$ to $8500\text{\AA}$ while maintaining constant cell pressure. Figure 1 is a typical spectrum. The pressure was changed by

adding additional reactant (ozone or quenching gas) and another spectrum recorded. This method was useful for obtaining low-pressure spectral information and rotational temperatures but for rate constant determinations it yielded too little pressure dependent data. (2) The second method was to observe changes in emission intensity of selected lines from the hydroxyl spectrum while reactant pressure was slowly increased. Figure 2 is a typical experimental trace. This method yielded excellent continuous pressure dependent data. The outputs from the SSR ratemeter and from the Datametrics pressure transducer were fed into the two channels of a paper tape punched interface and punched at four second intervals. Reactant pressure was varied by a factor of about one hundred to a maximum cell pressure of 0.1 Torr.

A. Determination of Vibrational Populations

The technique used here is similar to that used by Gabelnick¹⁵ for the IF molecule and by Hancock and Smith¹⁶ for the CO molecule. The method involves computing a synthetic spectrum using the known spectroscopic quantities for hydroxyl and then correcting for the spectrometer slit function, detector response, and the RC time constant of the

detection system. The synthetic spectrum is then fitted to an 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, but an estimate for a Boltzmann rotational temperature is needed.

The intensity of a spectral line in emission is

$$I_{\nu'' J''}^{\nu' J'} = \frac{64\pi^4 \nu^3 B_{\nu'} S_{J''}^{J'} N_{\nu'}}{3 h k T_r} \exp \left[\frac{-B_{\nu'} J'(J'+1)}{k T_r} \right] |R_{\nu''}^{\nu'}|^2 \quad (3)$$

where ν is the radiation frequency, $B_{\nu'}$ is the rotational constant for vibrational level ν' , $S_{J''}^{J'}$ is the rotational line strength (a term involving overlap of rotational wave functions in the transition matrix), $N_{\nu'}$ is the population number of the upper vibrational state ν' , T_r is rotational temperature, and $|R_{\nu''}^{\nu'}|^2$ is the vibrational contribution to the transition matrix.¹

The rotational line strength factors $S_{J''}^{J'}$ have been calculated for hydroxyl¹⁷ assuming a coupling model intermediate to Hund's cases a and b. The relative transition matrix elements used in this calculation are those calculated by Cashion.¹⁸

The frequency term ν in (3) is the difference in frequency between the initial and final vibration-rotation states. The term may be simply calculated using spectroscopic constants^{19,20} and the rotational term values calculated by Hill and Van Vleck²¹ for a case intermediate to Hund's cases a and b. However the resultant expression is very bulky and will not be written here.

The hydroxyl radical electronic ground state is a doublet, $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$. Each of these multiplets has three branches in emission (R, $J'' = J' - 1$; Q, $J'' = J'$; P, $J'' = J' + 1$). Because rotational line strengths were known up to $J' = 41/2$ the synthetic spectrum was calculated by summing each branch of each multiplet up to $J' = 41/2$. Line strengths for transitions between the multiplets were negligible.

All terms in (3) are then known or calculated except the vibrational population distribution, so a synthetic spectrum may be calculated assuming unit vibrational populations. Figure 3 shows three such synthetic spectra calculated at different assumed rotational temperatures.

The relative intensity of each band was calculated at one Angstrom intervals over its entire wavelength range. A synthetic spectrum was then obtained by summing, over the region $5000\overset{\circ}{\text{A}} - 8500\overset{\circ}{\text{A}}$, the intensities of all contributing bands at each one Angstrom wavelength interval. Relative vibrational populations were determined from a set of decay curves, such as illustrated in Figure 2, by fitting the relative band contributions to the total observed intensity with the set of relative vibrational populations serving as fitting parameters. Table I lists peaks in the hydroxyl spectra and the bands which contribute to each peak. Table II shows the relative contribution of each band to the peak. The peaks for which wavelength λ , is underlined are those which were most commonly observed.

B. Evaluation of Reaction Rate Constants

This procedure yielded sets of populations for the six observed vibrational levels ($4 \leq v \leq 9$) over the entire pressure range of the experiment. A number of processes are significant in populating or depopulating the general vibrational state v :

Formation processes

Reaction of hydrogen atoms with ozone

Collisional cascading from levels above

Radiative transitions from levels above

Destruction processes

Radiative transitions to levels below

Collisional cascading to levels below

Deactivation at the wall

Reaction with ozone

Hydroxyl losses by pumping out of the system, by hydroxyl-hydroxyl reaction, or by self absorption of radiation were held to negligible levels by low pumping speed and low total hydroxyl concentrations. This model may be described by (4)

$$[\text{HO}]_v = \frac{f_v k_1 [\text{H}][\text{O}_3] + \sum_{v'=v+1}^9 \tau_{v',v}^{-1} [\text{HO}]_{v'} + k_q^{v+1,v} [\text{HO}]_{v+1} [\text{M}]}{\tau_v^{-1} + k_2^v [\text{O}_3] + k_q^v [\text{M}] + k_w/[\text{M}]^{\frac{1}{2}}} \quad (4)$$

where f_v is the fraction of hydroxyl produced in vibrational level v , and the other terms are defined in Table III.

Quenching at the wall was assumed to be total, so the wall quenching constant becomes a measure of how rapidly a molecule moves to the wall and was assumed to be identical for all vibrational levels. Because vibrational state $v=9$ is populated only by chemical reaction, an initial increase in intensity at low pressure as $[\text{M}]$ is increased must be attributed to a decrease in the rate at which molecules are quenched at the wall. If reactant ozone is in sufficient excess over inert quencher M , (4) may be written in terms of the intensity of the $v=9$ to $v=4$ transition

$$\frac{1}{I_{9,4}} = \frac{\tau_9^{-1} + k_2^9 [O_3] + k_w^9/[M]^{\frac{1}{2}}}{\tau_{9,4}^{-1} f_9 k_1 [H] [O_3]} \quad (5)$$

At low pressures, a plot of $1/I$ versus $1/[M]^{\frac{1}{2}}$ yields a straight line, and the ratio of slope to intercept is $k_w/(\tau_9^{-1} + k_2^9 [O_3])$. On the basis of known τ_9^{-1} and a preliminary value of k_2^9 , the value of k_w was determined to be about $1.7 \times 10^8 \text{ sec}^{-1} (\text{molecules/cm}^3)^{\frac{1}{2}}$. A later measurement of k_2^9 yielded a value of k_w within the original error limits, so k_w was not revised.

The first term in the numerator of (4) includes the hydrogen atom concentration, which could not be measured in this system. There are two sources of hydrogen atoms in this system: primary, those produced by the microwave discharge; secondary, those produced by the reaction of hydroxyl with ozone. The possible products of the reaction of $HO(v)$ with ozone are

The partitioning between these three paths is unknown. The steady-state concentration of hydrogen atoms is

$$[H] = \{F + [O_3] k_3 \sum_{v=4}^9 [HO(v)]\} / k_1 [O_3] \quad (6)$$

where F is the in-flow rate of hydrogen atoms and k_3 is the unknown, average function

$$k_3 = \sum_{v=0}^9 k_3^v [HO(v)] / \sum_{v=4}^9 [HO(v)] \quad (7)$$

In studies of the rate of reaction, $\text{HO}(v) + \text{O}_3$, the concentration of ozone was set sufficiently high that the chemical reaction was much faster than the quenching terms in (4), which reduces to the form

$$[\text{HO}(v)] = \frac{x_1^v + x_2^v [\text{O}_3] \sum_{v'=v+1}^9 [\text{HO}(v')] + \sum_{v'=v+1}^9 \tau_{v,v'}^{-1} [\text{HO}(v')]}{\tau_v^{-1} + k_2^v [\text{O}_3] + k_w/[M]^{\frac{1}{2}}} \quad (8)$$

where $x_1^v = F f_v$ and $x_2^v = k_3 f_v$. Three parameters were evaluated from the data, x_1^v , x_2^v and k_2^v . Typically 15 to 20 sets of data, observed $[\text{HO}(v)]$, $[\text{O}_3]$ and $[M]$, were used so that the system was highly overdetermined. The parameters were varied to minimize the function

$$G = \sum ([\text{HO}(v)]^{\text{OBS.}} - [\text{HO}(v)]^{\text{CALC.}})^2 \quad (9)$$

C. Evaluation of Vibrational Deactivation Constants

All the terms in (4) are known either from the literature or from measurements in this laboratory except the terms f_v , $[\text{H}]$, $k_q^{v+1,v}$, and k_q^v . However f_v and $[\text{H}]$ are inseparable because hydrogen atom concentration was held constant in the series of experiments studying vibrational quenching. This reduces the number of unknowns to three. Because vibrational level nine is the highest level populated, there is no quenching term in the numerator when the equation is written for level nine. Since the model limits quenching to one-quantum steps, the rate at which state nine is quenched is identical to the rate at which state eight is populated by quenching. If each level is solved sequentially from state nine down, there remain but two unknowns in (4). Typically 15-20 population-versus-pressure points were used for each determination.

The two unknowns were varied until (9) was minimized.

Single quantum transitions are expected to be the dominant quenching process for several reasons. The $\Delta v=4,5$ and 6 radiative transitions observed in this work have first order rate constants on the order of $1.0 \times 10^{-2} \text{ sec}^{-1}$ while $\Delta v=1$ transitions for hydroxyl have first order rate constants²² of approximately 10 sec^{-1} . Collisional transitions are expected to have relative probabilities similar to radiative transitions, so multiquantum processes would be very slow compared to single quantum processes. Also, current energy-transfer theories predict at most a ten percent contribution of $\Delta v=2$ transitions to an overall quenching rate²³.

The initial relative vibrational populations produced by reaction (1) may be determined by following emission to as low a pressure as possible. As the pressure in the cell is lowered, the wall quenching term in (4) becomes the dominant loss process, limited by the speed of migration to the walls. At zero pressure (4) is reduced to

$$[\text{HO}]_v = \frac{f_v k_1 [\text{H}][\text{O}_3]}{(\text{wall quenching rate constant})} \quad (10)$$

Thus the fraction, f_v , is directly proportional to the extrapolated population at zero pressure.

Results

Chemical rate constants, k_2^v - One quantity always of interest when dealing with chemically activated species is the temperature which characterizes the rotational distribution. In this work an approximate rotational temperature was determined by finding which of several synthetic spectra (calculated with different T_r) best fit the observed spectrum. This can be understood by noting the considerable dependence of band shape on temperature illustrated in Figure 3. It was determined

that a 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 rotational temperature was found to persist to the high pressure end of the experiments, though the maximum 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 is expected to undergo 300-500 collisions during its lifetime and there was evidence in this work that rotational relaxation was indeed occurring. Murphy²⁴, 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, Polanyi²⁸ found that a temperature of approximately 2000°K best described the rotational distribution.

The results found for the reaction of HO(v) with O₃ are shown in Table IV. The rate constants found in this work are almost uniformly 40% higher than those reported by Coltharp et al¹⁰. This difference can probably 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 within a vibrational level would be expected to lead to an increase in the reaction rate constant.

The reaction of HO and O₃ can lead to a variety of products: H + O₂ + O₂ (v ≥ 1); HO + O₂ + O (v ≥ 3); HO₂ + O₂ (v ≥ 0). 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. 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 earlier, this reaction path was compensated for by the parameter x_2 which was an "average" rate constant for $\text{HO}(v=4-9)$ reacting to produce secondary H atoms. Because the value of this parameter comes as a result of a fit to experimental data, 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 much significance to this number beyond noting that it seems to indicate that the reaction to produce secondary hydrogen is not particularly favored.

As seen in Table IV there is a large increase in k_2 between $v=5$ and $v=6$. This may be due to the onset of the second reaction listed above. The existence of another reaction channel which becomes energetically favorable would certainly increase the total rate constant.

Anderson and Kaufman²⁶ report a value of $5 \times 10^{-14} \text{ cm}^3/\text{molec-sec}$ for the reaction $\text{HO}(v=0) + \text{O}_3 \rightarrow \text{HO}_2 + \text{O}_2$ at room temperature. There is no theoretical basis for extrapolation of the present data to $v=0$. If only the results for $v=4$ and $v=5$ are extrapolated to $v=0$, a value of $5 \times 10^{-13} \text{ cm}^3/\text{molec-sec}$ is found. However this may not be unreasonable because the values for $v=4$ and 5 are based on an elevated rotational temperature and presumably three reaction channels. Anderson and Kaufman's value at $v=0$ is based on low rotational temperature and only one reaction channel.

A test of the steady state model and of the parameters determined by that model is to examine the goodness of the fit. The function (9), which was minimized, was the sum of the squares of the differences between an observed HO population and a calculated HO population. In a typical experiment, this model was able to fit sixteen different populations for each of the six observed vibrational levels to within an average of less than four percent.

Vibrational deactivation rate constants, k_q - In figures 4a, b are plots of vibrational populations versus pressure extrapolated to zero pressure with M gases being Ar and O₂, respectively. A summary of the results for initial vibrational population distribution are presented in Table V. In cases where the intercept was negative, f_v was set equal to zero. A negative intercept is a common artifact of the uncertainties in following a multilevel system. Both Harrison⁵ in his observation of the airglow and Hancock et al²⁷ in observing CO chemiluminescence compute negative rates of activation for some vibrational levels. A comparison of these results with other results obtained through a wide variety of experimental techniques is shown in Table VI. 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 which characterizes the vibrational population distribution. Given any two relative vibrational populations, the temperature which characterizes their ratio is

$$T_{\text{vib}} = - (\epsilon_i - \epsilon_j) / k \ln(N_i / N_j) \quad (11)$$

where N_i and N_j are the relative population, ϵ is the energy of the vibrational level and k is the Boltzmann constant. Typical relative populations and the pressures at which they were observed are listed in Table VII. If $N_{v+1} > N_v$ 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 a temperature of $\sim 20,000^\circ\text{K}$ whereas the N_6/N_5 ratio yields a temperature of $\sim 5600^\circ\text{K}$. The higher pressure distribution with H_2 very roughly fits a Boltzmann distribution at $10,000^\circ\text{K}$. Naturally these estimates consider only up to $v=9$ because higher levels are not populated.

In other hydroxyl studies, Garvin and coworkers⁷, working at a total pressure of 2-5 Torr, found a vibrational temperature of $\sim 9250^\circ\text{K}$. Harrison calculated $T_{\text{vib}} = 10800^\circ\text{K}$ from an observation of the airglow⁵. Murphy²⁴ was unable to fit a Boltzmann temperature to his population observed at 4-8 Torr. Polanyi²⁸ reports a low temperature of 5000°K at a total pressure of 7×10^{-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°K).

The results of the quenching experiments are listed in Table VIII and illustrated in Figure 5. Again, because these quantities were derived by fitting observations to a model, it is significant to measure the goodness of the fit. When the sum of the squares of the residuals, (9), is minimized the average percentage deviation of the model from observation ranged from 5-20%, tending to increase with lower vibrational level. In this type of analysis, errors are known to

accumulate at lower v because the rate constants determined at high v are used in calculations for each successively lower vibrational level.

Judging from experimental scatter error limits should range from $\pm 20\%$ for $v=9$ to $\pm 50\%$ for $v=4$.

A question which may be raised is whether hydrogen molecules react at a significant rate with excited hydroxyls. The rate constant for the zero vibrational level reaction has been measured at room temperature and reported²⁹ to be $7.1 \times 10^{-15} \text{ cm}^3/\text{molec-sec}$. As it does with ozone, excited hydroxyl might be expected to react much faster with hydrogen. However, several pieces of evidence point to the conclusion that if this is true, the reaction is still not sufficiently fast to compete with quenching.

It was observed in the lower vibrational states, particularly $v=4$ and 5 , that there was an initial rise in population upon addition of a quenching gas to the system. This rise is due to the state being populated faster by cascading processes than it is being depopulated by quenching. This phenomena was observed to be of nearly equal magnitude for all quenching experiments; H_2 , N_2 , O_2 , etc., whereas it was not observed with ozone which is known to undergo a chemical reaction.

Another indication is that the proposed model fits observations quite well. The model specifically requires quenching in one-quantum steps and any excited hydroxyl which reacts would be removed from the manifold of states, resulting in a poorly fitting model. Finally if the reaction with hydrogen were to occur, 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 vibrational levels which are populated by the hydrogen atom ozone reaction. That the rate constants for $v=8$ and 9 are higher for quenching with hydrogen than with deuterium indicates that this does not happen.

DISCUSSION

Energy Transfer

Quenching of vibrationally excited hydroxyl radicals by argon must be accomplished by a vibration to translation energy transfer process because argon has no other degrees of freedom available. This process is expected to be slow because it is assumed that one vibrational quantum which is many times greater than kT must be absorbed into translation. For this reason Ar is often used at relatively high pressures in reaction systems as a carrier gas or to retard diffusion toward the walls. The present results indicate that quenching by Ar is slower than with the other quenching gases used, but it is by no means negligibly slow.

Assuming that one full vibrational quantum must be converted to translation, the present results for quenching with Ar are much faster than would be predicted for the $v=1 \rightarrow v=0$ transition by vibration-translation (V-T) energy transfer theory³⁰⁻³². These theories, based on short range exponential repulsion, predict probabilities which increase at higher vibrational levels and which are highly dependent on the amount of energy which must be converted from vibration to translation. The exact classical mechanical calculation of Kajimoto and Fueno³³ raises the possibility that V-T energy transfer probability is not a simple monotonically increasing function of vibrational level. They report finding an increase in transfer efficiency with vibrational level to

a maximum followed by a decrease in efficiency as the dissociation limit approached. Moreover, it is not uncommon for researchers to find that quenching by atoms is relatively efficient. Stephenson³⁴ found that He was more efficient than CO in quenching $\text{CO}(v=1)$ and that it was only a factor of four less efficient than O_2 . Myers et al³⁵ found that Ar was more efficient than H_2 and nearly as efficient as N_2 or O_2 in quenching NO_2 fluorescence (electronic excitation).

Recalling the high rotational temperature characteristics of this work, it means that there was a relatively even distribution of population in all rotational levels up through $J=25/2$. This distribution persisted both at higher pressures and in the lower vibrational levels. If large ΔJ transitions are assumed possible, vibrational relaxation of hydroxyl may occur with a relatively small energy transfer. For instance, a transition from $V=8, J=5/2$ to $v=7, J=25/2$ has an energy separation of only 370 cm^{-1} compared to the 2400 cm^{-1} separation between rotationless $v=7$ and $v=8$ levels.

The other quenching gases used in this work were all diatomics ($\text{O}_2, \text{N}_2, \text{H}_2, \text{D}_2$). With these gases it is expected that a vibration to vibration (V-V) energy transfer process occurs in which only the energy defect (the difference in energy between the hydroxyl vibrational quantum and the quenching gas vibrational quantum) must be absorbed into translation. From the following simple qualitative comparison it may be reasoned that the rates of V-V energy transfer in the hydroxyl radical system should be somewhat slower, but quite similar to those of the hydrogen fluoride system and much faster than those of the carbon monoxide system.

CO	HO	HF
low vibrational frequency	high vibrational frequency	higher vibrational frequency
small rotational spacing	large rotational spacing	larger rotational spacing
weak attractive forces	strong attractive forces	strong attractive forces
dipole moment = 0.1D	dipole moment = 1.70D	dipole moment = 1.9D

Some results obtained by similar experimental technique for all three molecules also serve to place hydroxyl quenching behavior close to that of HF. Measured rate constants for quenching CO ($4 \leq v \leq 13$) with a variety of species were typically in the range of 10^{-14} cm³/molecule-sec except for those cases of near resonant exchange¹. For HF ($v \leq 5$) being quenched by HF or CO₂ rate constants are on the order of 10^{-12} cm³/molecule-sec or faster³⁹. The results of this work place the rate constants for HO ($4 \leq v \leq 9$) near 5×10^{-13} cm³/molec-sec.

Worley has reported rates of interaction for HO ($v=9$) plus a variety of gases³⁶. The reported rate constants (HO($v=9$) + O₂, 1.0×10^{-14} cm³ molec-sec; HO ($v=9$) + N₂, 3.6×10^{-15} cm³/molec-sec) are extremely low. Worley also reports that the rate constant for quenching with O₂ is independent of HO vibrational level³⁷. The low rate constants and lack of dependence on vibrational level do not at all agree with the expected trends for the hydroxyl radical. Further, Basov and coworkers³⁸ have derived an average value of $(5 \pm 2.5) \times 10^{-13}$ cm³/molec-sec for the rate constant for transfer of energy from DO⁺ to CO₂ in a CO₂ laser. Since

DO^+ should be quenched faster than HO^+ , this value might seem low, but Airey and Smith³⁹ note that the Basov value for DF^+ 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 for CO_2 deactivating $\text{HO}(v=9)$.

The theories of V-V transfer considering only short range interactions^{32,40-42} have shown success for many non-hydride molecules but generally predict probabilities much lower than measured for hydrogen halides. These theories again predict a very steep dependence on the energy defect and if they consider rotational transitions, restrict them to $\Delta J=1$. There is a large body of V-V which suggests that energy transfer is due to long range interactions. These may be dipole-dipole coupling^{43,44} or higher order multipole coupling^{45,46} and the theory has been extended with good success to non-resonant V-V transfer in CO relaxation⁴⁷. However, these theories still cannot account for the very rapid rates measured for HF and DF relaxation⁴⁸⁻⁵⁰.

There remain two approaches, though, which seem to promise some measure of success in explaining rapid vibrational relaxation in the hydroxyl radical. The fact that a highly excited rotational distribution is present even in the lower vibrational levels makes it seem likely that considerable energy is absorbed into rotation in order to reduce the energy defect. This requires a theory in which there are no ΔJ restrictions, an idea also recognized by Stephens and Cool⁵⁰. Dillon and Stephenson^{51,52} have formulated a theory in which they can evaluate the elements of the scattering matrix to all orders. As in the Sharma-Brau theory they use a multipole expansion of the intermolecular potential,

but they make none of the usual Born approximations⁵³. They compare their calculations with the experimental data of Airey and Smith³⁹ on HF relaxation and find agreement within the error estimates of their theory. Most interesting is that they find $\Delta J=7$ to be the most probable transition between initial and final rotational states of HF.

An area of speculation in V-V theory which would allow large ΔJ is the influence of strong attractive forces such as hydrogen bonding (estimated well depth of 2-4 kcal/mole) or dimer formation in HF. There is little doubt that an attractive potential, whether it is responsible for a very short lived intermediate complex, for causing favorable orientation of collision partners, or for causing the colliding molecules to travel on curved trajectories would significantly increase the efficiency of V-V transfer. Several researchers^{39,50,54,55} have suggested attractive potentials as a possible explanation for very high rates of V-V transfer. It seems highly likely that in this system in which a free radical (HO) is being quenched that some form of attractive chemical interaction and large ΔJ transitions are responsible for very efficient vibrational relaxation.

Stratospheric Application

The present results for reaction with ozone and quenching by nitrogen and oxygen, have been applied to a computational model of the stratosphere to determine the role of excited hydroxyl radicals up to an altitude of 48 kilometers. For simplicity, the models studied here only include chemistry of the O_x and HO_x systems. The results are not considered to be absolute because of approximations made for the rate constants for reactions of excited species. However the results are adequate to

determine the relative importance of excited hydroxyl reactions compared to ground state hydroxyl reactions.

Calculations were made with a chemical kinetics package written by Whitten¹¹, modified for stratospheric modelling by including time, elevation, latitude and solar spectrum parameters. Hydroxyl radicals in the stratosphere were investigated by three different models.

1. Ground state model - In this model all reactions which produce hydroxyl radicals are assumed to produce them in the lowest vibrational state only. This is equivalent to instantaneous quenching. The reactions considered are listed below.

Rate constants were obtained from reference 56. Photolysis rates were calculated by the program with absorption cross sections available from the literature. Rates for reactions (R14) and (R17) were set to zero in this model. Reaction (R20) actually produces H_2O_2 , but it was

assumed that this was rapidly photolyzed.

2. Basic excited hydroxyl model - The same basic reaction scheme was used except reaction (R13), was partitioned to produce excited hydroxyls in vibrational levels four through nine. Reaction (R14) was allowed for vibrational levels three through nine and reaction (R15) was allowed for vibrational levels zero through two. The quenching reaction (R17) was assigned rate constants for each level which were 80% of the rate constant for N_2 quenching plus 20% of the rate constant for O_2 quenching. Rate constants for other reactions of excited hydroxyls were approximated by assigning the rate constant for reaction of vibrational level nine to be one order of magnitude greater than for reaction of ground state hydroxyl. Rate constants for intermediate levels were scaled appropriately. For reaction (R19) the rate constant for vibrational level nine was assigned to be only 2.5 times larger because of the extremely rapid ground state reaction.

3. Maximum excited hydroxyl model - In this model other reactions which yield hydroxyl radicals were assumed to produce vibrational excitation as follows:

Reaction (20a) assumes photolysis of H_2O_2 at 205 nm.

All the calculations reported here were made with a midday spring-time sun at 45°N latitude. Hydroxyl radical concentrations, in multiples

of 10^6 , as a function of elevation in the first model are:

Elevation (km)	28	33	38	43	48
HO (molecules/cm ³)	2.1	3.7	7.7	10.	7.2

For comparison, at 48 km., other concentrations are O₃, 1.2(11); O(³P), 8.1(9); O(¹D), 5.3(2). Instantaneous rates for hydroxyl radical reactions may be seen in Table IX. It is evident that at the higher elevations, formation and destruction of hydroxyl proceeds primarily through O(³P) reactions. Ozone reactions are secondary. For instance, examining the instantaneous rates of those reactions in which ozone is destroyed, we see that ground state hydroxyl is of minimal importance.

<u>Reaction</u>	<u>Instantaneous Rate at 45 km.</u>
O ₃ + HO	3.6(4) molecules/cm ³ -sec
O ₃ + H	6.2(5) "
O ₃ + HOO	2.2(3) "
O ₃ + O(³ P)	3.9(6) "
O ₃ + hv	8.9(8) "

In the two models allowing production of vibrationally excited hydroxyl radicals, it was found that quenching was extremely rapid and thus limited the steady state population of excited hydroxyls.

<u>Excited Hydroxyl Populations at 48 km</u>						
<u>Model \ V</u>	9	7	5	3	1	0
2	1.9(1)	3.0(1)	9.5(1)	5.7(2)	3.2(3)	7.2(6)
3	1.9(1)	3.0(1)	3.9(2)	2.3(3)	1.3(4)	7.2(6)

The rapid quenching is illustrated for both models by the following instantaneous rates for vibrational level nine at 48 km.

<u>Reaction</u>	<u>Instantaneous Rate</u>
$\text{HO}(v=9) + \text{O}({}^3\text{P})$	6.1(1) molecules/cm ³ -sec
$\text{HO}(v=9) + \text{O}_3$	2.6(1) "
$\text{HO}(v=9) + \text{M}$	2.2(5) "

The total rates of hydroxyl radical reaction with ozone at 48 km. are 3.4% and 13% faster for models 2 and 3 respectively than for model 1, but this is not sufficient to make the hydroxyl reaction with ozone significant at that elevation. At lower elevations where the hydroxyl reaction with ozone is more important, there are too few excited hydroxyls to have any effect.

In another set of calculations in which the total ozone column was calculated for each hour from sunrise to sunset, the column remained unchanged by either model for vibrationally excited hydroxyl radicals. Due to the very rapid quenching it is also safe to assume that excited hydroxyls have no significant effect on the night-time chemistry of the stratosphere. The night-time airglow, which indicates the presence of vibrationally excited hydroxyl radicals, originates in the mesosphere at 80-90 km. At 90 km. atmospheric pressure is down by a factor of 500 from that at 50 km. so the lifetime and hence importance of vibrationally excited hydroxyl radicals would be much greater.

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Table I. Hydroxyl Spectra Peaks and their Band Composition

	$\lambda (\text{\AA})$	<u>Bands</u>				
1	5553			7-1	6-0	
2	5879		8-2	7-1	6-0	
3	6071		8-2	7-1	6-0	
4	6147		8-2	7-1	6-0	5-0
5	6189		8-2	7-1		5-0
6	6252	9-3	8-2	7-1		5-0
7	6470	9-3	8-2		6-1	5-0
8	7609	9-3				
9	6837	9-3	8-2	7-2	6-1	5-0
10	7087	9-3		7-2	6-1	
11	7250	9-3	8-3	7-2	6-1	
12	7478	9-3	8-3	7-2	6-1	4-0
13	7528		8-3	7-2	6-1	4-0
14	7577		8-3	7-2	6-1	4-0
15	7632		8-3	7-2	6-1	4-0
16	7723	9-4	8-3	7-2		4-0
17	7858	9-4	8-3	7-2		5-1 4-0
18	8147	9-4	8-3	7-2		5-1 4-0
19	8289	9-4				5-1 4-0

Table II. Hydroxyl Peaks and Relative Band Contribution ($T_R=1500^\circ\text{K}$)

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

NOTE: $1.98(2) = 1.98 \times 10^{-2}$

Table III. Chemical Reactions and Rate Constants

(1) $\text{H} + \text{O}_3 \rightarrow \text{HO} (v \leq 9) + \text{O}_2$	k_1
(2) $\text{HO}(v) + \text{O}_3 \rightarrow \text{products}$	k_2^v
$\text{HO}(v') \rightarrow \text{HO}(v) + h\nu$	$\tau_{v'v}^{-1}$
$\text{HO}(v) \rightarrow \text{HO} + h\nu$	τ_v^{-1}
$\text{HO}(v+1) + \text{M} \rightarrow \text{HO}(v) + \text{M}$	$k_q^{v+1,v}$
Wall deactivation	k_w

Table IV. Rate Constants for Reaction of $\text{HO}(\nu) + \text{O}_3$,
 $k_2^v \times 10^{12}$ ($\text{cm}^3/\text{molecule-sec}$).

Exp \ ν	<u>9</u>	<u>8</u>	<u>7</u>	<u>6</u>	<u>5</u>	<u>4</u>
1	11	9.4	8.6	7.4	4.6	3.8
2	11	9.0	8.8	7.2	4.5	3.8
3	10	8.5	8.2	6.8	4.3	3.5
4	11	8.7				
5	12	8.9	8.3	7.1	4.7	3.7
Avg:	11	8.9	8.5	7.1	4.5	3.7
Mean Deviation:	$\pm .40$	$\pm .24$	$\pm .23$	$\pm .18$	$\pm .13$	$\pm .10$

Table V. Relative Initial Vibrational Population Distributions

<u>M. gas</u>	<u>f₉</u>	<u>f₈</u>	<u>f₇</u>	<u>f₆</u>	<u>f₅</u>	<u>f₄</u>
Ar	1.0	.81	.43	0	.23	0
Ar	1.0	.52	.02	.10	.40	.27
H ₂	1.0	.83	.57	.51	.26	.15
N ₂	1.0	.52	.60	0	0	0
O ₂	1.0	1.01	.08	0	0	0
D ₂	1.0	.68	.49	.43	.20	0
Avg.	1.0	.73	.37	.17	.18	.07

Table VI. Comparison of Recent Determinations of Relative Initial
Vibrational Distribution.

<u>f₉</u>	<u>f₈</u>	<u>f₇</u>	<u>f₆</u>	<u>f₅</u>	<u>f₄</u>	<u>f₃</u>	<u>f₂</u>	<u>Reference</u>
1.0	.87	.50	.40	.35	.32	.26		8
1.0	.25	0	0	0	0	0	0	7
1.0	1.14	.17	0	.10	.21	-0.8		4
1.0	.73	.37	.17	.18	.07			This work

Table VII. Typical Vibrational Population Distributions (normalized to $N_4=1.0$).

M gas	Pressure (Torr)	N_4	N_5	N_6	N_7	N_8	N_9
Ar	6×10^{-4}	1.0	.40	.19	.18	.24	.20
D ₂	10×10^{-4}	1.0	.60	.30	.25	.32	.28
N ₂	11×10^{-4}	1.0	.14	.07	.05	.06	.06
Ar	60×10^{-4}	1.0	.14	.10	.14	.26	.17
H ₂	59×10^{-4}	1.0	.78	.28	.19	.23	.22

Table VIII. Rate Constants for $\text{HO}(\nu) + \text{M}$, k_q ($\text{cm}^3/\text{molecule-sec}$) in units of 10^{-13} .

ν / M	Ar	O_2	N_2	H_2	D_2
9	1.1	3.5	4.4	5.8	4.9
8	1.1	5.4	3.7	7.4	6.4
7	2.2	7.8	5.5	8.0	11
6	2.9	7.3	5.0	7.0	8.6
5	1.5	3.2	2.1	4.0	4.3
4	.079	1.4	.78	1.8	2.0

Table IX. Instantaneous Rates of Hydroxyl Radical Reactions in the Stratosphere (molecule/cm³-sec).

<u>Elevation (km)</u>	<u>Formation Reactions</u>				<u>Destruction Reactions</u>			
	<u>7</u>	<u>11</u>	<u>13</u>	<u>16</u>	<u>20</u>	<u>10</u>	<u>15</u>	<u>19</u>
28	2.6(4)	2.3(4)	9.7(0)	9.4(4)	1.2(4)	4.0(3)	1.6(5)	2.6(4)
33	4.2(4)	1.1(5)	2.6(3)	6.7(4)	1.1(4)	3.5(4)	2.1(5)	4.2(4)
38	6.4(4)	5.4(5)	7.5(4)	3.8(4)	6.6(3)	4.2(5)	3.2(5)	6.4(4)
43	6.1(4)	1.7(6)	5.2(5)	1.2(4)	3.8(3)	2.1(6)	1.7(5)	6.2(4)
48	2.5(4)	1.9(6)	6.2(5)	2.2(3)	1.5(3)	2.5(6)	3.6(4)	2.6(4)

<u>Reactions</u>			
$O(^1D) + H_2O \rightarrow 2HO$	(7)	$HOO + HOO \rightarrow 2HO + O_2$	(20)
$O(^3P) + HOO \rightarrow HO + O_2$	(11)	$O(^3P) + HO \rightarrow O_2 + H$	(10)
$O_3 + H \rightarrow HO + O_2$	(13)	$O_3 + HO \rightarrow HOO + O_2$	(15)
$O_3 + HOO \rightarrow HO + 2O_2$	(16)	$HO + HOO \rightarrow H_2O + O_2$	(19)

2.6(4) = 2.6×10^4

Titles to Figures

- Figure 1 - An observed spectrum, with hydroxyl overtone emission bands identified.
- Figure 2 - Decay of intensity at 7250 $\text{\AA}$.
- Figure 3a - Unit synthetic spectrum with a rotational temperature of 600°.
- Figure 3b - Unit synthetic spectrum with a rotational temperature of 1500°.
- Figure 3c - Unit synthetic spectrum, with a rotational temperature of 2500°.
- Figure 4a - Vibrational populations extrapolated to zero pressure, Argon as M gas.
- Figure 4b - Vibrational populations extrapolated to zero pressure, O₂ as M gas.
- Figure 5 - Rate constants for quenching as a function of hydroxyl vibrational level.

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