

Energy partitioning in O(1 D 2) reactions. II. O(1 D 2)+CH₄→OH(v')+CH₃

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Energy partitioning in $O(^1D_2)$ reactions. II. $O(^1D_2) + CH_4 \rightarrow OH(v') + CH_3$

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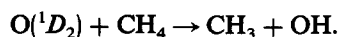
The complete OH vibrational distribution created by the reaction of $O(^1D_2)$ with CH_4 has been recorded directly, using low pressure infrared emission spectroscopy. The result shows that the energy is partitioned nonstatistically into this degree of freedom. The population of $OH(v' = 2)$ is approximately equal to or slightly greater than that of $OH(v' = 1)$ under the conditions of this experiment and substantial populations are recorded from all levels up to $OH(v' = 4)$, the maximum allowed by the exoergicity of the reaction.

I. INTRODUCTION

The chemistry of the ozone layer is partly determined by reactions between $O(^1D_2)$ and small hydride molecules, which are transported into the stratosphere by vertical mixing from the troposphere.¹ Most of these reactions produce OH radicals. If they occur in the region of high ozone concentration at altitudes from about 20 to 50 km, the OH can cause the catalytic destruction of very large quantities of ozone via the HO_x cycle.^{2,3}

Methane is particularly important in this respect. It is produced in large quantities by terrestrial biological sources and has a very long photochemical lifetime (≈ 1 year at altitudes below about 70 km).¹ For these lower altitudes, the characteristic times for vertical transport by wind and vertical eddy diffusion are somewhat less than the photochemical lifetime, with the result that CH_4 is transported into the stratosphere^{4,5} where it can react with the $O(^1D_2)$ produced by solar O_3 photolysis.

The reaction between $O(^1D_2)$ and CH_4 is extremely fast; reported rate constants lie between 1.5 and 4.0×10^{-10} $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.⁶ More than 96% of the total $O(^1D_2)$ removal by methane is reactive⁷:



The overall exoergicity (ΔH_0°) of this reaction is⁸ -180 kJ mol^{-1} .

In addition to this reaction there are two other, chemically different, channels possible—one producing $H + CH_3O$, the other $H_2 + H_2CO$. These are -138 and -481 kJ mol^{-1} exoergic, respectively. Despite the large exoergicity of the last channel, a recent molecular beams study⁹ showed that it constitutes a negligibly small fraction of the reaction. Channel (1) accounts for more than 80% of the reaction^{6(e)}; the remainder is H atom elimination.⁹

Early gas phase photochemical studies of this reaction^{6(b),6(c)} showed that the main products at low pressures are CH_3 and OH. At high pressure,^{6(b)} or in liquid Ar,^{6(a)} the insertion product, CH_3OH was stabilized. Similar studies of $O(^1D_2)$ reactions with slightly larger hydrocarbon molecules¹⁰ also showed that the insertion product is stabilized under high pressure conditions. Radical scavenging techniques showed that the production of radicals becomes important at low pressure.

Based on the evidence that the insertion product is stabilized at high pressure, the direct abstraction was thought to

make only a minor contribution. Nevertheless, previous work had provided substantial evidence for its existence. OH with vibrational excitation up to $v' = 2$ has been detected following the flash photolysis of ozone in the presence of methane.¹¹ Also, studies based on the photolysis of N_2O in the presence of CH_4 found¹² that at pressures slightly above 1 atm the formation of CH_3OH was completely suppressed when the CH_3 radicals were scavenged by the addition of NO.

A recent laser-induced fluorescence study of this reaction¹³ found that the populations of the $OH(v' = 0)$ and $OH(v' = 1)$ levels were approximately equal and that the rotational excitation within each of these vibrational levels was very high. Both of these product modes had considerably more excitation than would be provided by the statistical decomposition of an excited CH_3OH reaction intermediate. It was reasoned that the observed result was produced by prompt, non-RRKM decomposition of an insertion intermediate. The conclusion that rotationally excited OH is produced by an insertion mechanism is based on an analogy with the $O(^1D_2) + H_2$ reaction. Similar (high) rotational excitation was measured by LIF studies of this reaction¹⁴ and good agreement with this result was obtained in classical trajectory calculations¹⁵ of the same process. The latter indicated that, on decomposition, the bending mode of an excited HOH intermediate could be converted to OH rotation.

We have recently developed a low-pressure infrared emission experiment capable of measuring the OH vibrational distributions produced by the reactions of $O(^1D_2)$ with hydrides. Our initial results show extensive vibrational excitation from the reactions with H_2 ^{16(a)} and H_2S .^{16(b)} We have recently completed a study of the CH_4 reaction, which we report here. The OH vibrational energy distribution observed in this case as well is found to have substantial vibrational excitation.

II. EXPERIMENT

The experiments were carried out in a low-pressure infrared chemiluminescence apparatus which had previously been used to measure the energy partitioning in reactions between F atoms and small free radicals.¹⁷ The main reaction chamber is a 25 cm diam by 25 cm high stainless steel cylinder evacuated through a 31 cm diam gate valve by a Varian VHS 400 diffusion pump. The reagents are introduced through two concentric quartz tubes located in the center of the reaction chamber lid.

Two different reagent inlets were used for the present experiments. The initial work was done with the same inlets used for our $O(^1D_2) + H_2$ study.^{16(a)} In this case, the reagents (ozone and methane) are premixed and enter through a 5 cm diam quartz tube in the reaction chamber lid. It was found that better mixing could be obtained at lower pressures by the use of a variable reagent inlet device previously developed for studies of F atom/free radical reactions.¹⁷ Most of the results reported here were obtained using the latter reagent inlet. In this case, ozone flows through a (2.5 cm diam) outer tube and methane is injected laterally into the ozone stream through a 1 mm high annular opening in the lower tip of (5 mm diam) concentric inner tube. Extensive modeling calculations reported in Ref. 17(b) have shown that efficient reagent mixing occurs at the location of this annular opening.

The $O(^1D_2)$ is generated by photolysis of ozone using a KrF excimer laser (Lumonics model 860-4) operated at a repetition rate of about 350 Hz. The laser beam is multipassed immediately beneath the lower ends of the reagent inlet tubes by two dielectric mirrors, coated for maximum reflectivity at 248 nm, and mounted facing each other in the vacuum chamber. The infrared emission from the internally excited OH is collected by a Welsh cell mounted with its axis perpendicular to and in the same vertical plane as that of the multipass laser mirrors. A Fourier transform spectrometer, optically matched to the Welsh cell, records the infrared spectrum.

In order to obtain adequate signal to noise, it was necessary to throttle the diffusion pump by partly closing the gate valve separating it from the reaction chamber. The measured total reagent inflow rates were in the range of $(4-6) \times 10^{-4}$ mol s⁻¹ for all experiments reported herein. The lowest pressure which gave adequate signal to noise was 1.1×10^{-2} Torr. Hence the pumping speed for this experiment had been throttled to about 850 ℓ/s (from the maximum baffled speed of 6000 ℓ/s). Assuming an effective volume of 1.5 ℓ for the Welsh cell, this indicates that the average residence time in the observation zone is $(1-2) \times 10^{-3}$ s. Since the time between gas kinetic collisions at this pressure is about 10^{-5} s, this indicates that the OH has 100-200 gas kinetic collisions in the observation zone.

The ozone used in these experiments was generated using a 15 kV silent-arc ac discharge apparatus of the conventional design¹⁸ which was built in this laboratory. Oxygen (Air Products, zero grade), purified by passing through a type 5A molecular sieve trap cooled to dry ice temperature, was passed through the electrode at a rate of about 0.1 ℓ/s at atmospheric pressure. The resulting mixture (approx. 5% O_3 and 95% O_2) flowed into a trap consisting of four helical coils of 50 mm diam Pyrex, each about 50 cm high by 30 cm diam, filled with silica gel and immersed in a dry-ice-cooled bath. The O_3 is efficiently retained by adsorption on the silica gel. We estimate that this trap is capable of storing between 5 and 10 mol of O_3 . Before each experiment, the trap is evacuated to a pressure of about 5 Torr for a few minutes in order to ensure that residual oxygen has been removed. The methane (Matheson, research grade) was used without further purification.

TABLE I. Experimental conditions and measured OH(v') product vibrational distributions.

Run	Pressure CH ₄	(mTorr) O ₃	Relative populations			
			$v' = 1$	$v' = 2$	$v' = 3$	$v' = 4$
1	10.0	10.0	0.46	0.31	0.18	0.05
2	8.0	3.0	0.32	0.34	0.21	0.13
3	5.6	5.5	0.27	0.33	0.26	0.14

III. RESULTS

OH distributions were measured as a function of total reagent pressure and O_3/CH_4 ratios. Roughly similar total reagent inflow rates were used in most cases; different total pressures were obtained by adjusting the gate valve used to throttle the diffusion pump. Three of the resulting distributions are listed in Table I, with the relevant experimental conditions. The first of these was measured using the reagent inlet configuration described in Ref. 16(a), the last two were obtained with the adjustable injector configuration described in the previous section. The less efficient mixing geometry of the older reagent inlet (expt. 1) required higher reagent pressures in order to obtain adequate signal to noise, hence the resulting vibrational distributions are more collisionally relaxed than those measured with the adjustable inlet.

The spectrum from which the populations for experiment 3 were calculated is shown in Fig. 1. This represents the poorest signal to noise (the lowest reagent pressures) used in the present study. The quantum number of the upper vibrational level is shown at the upper right corner of the figure. The rovibrational transitions of the individual Π doublets are indicated by a bifurcated line; the $^2\Pi_{3/2}$ ground state transition is at the left in each case.

The distributions are plotted in Fig. 2. The error bars

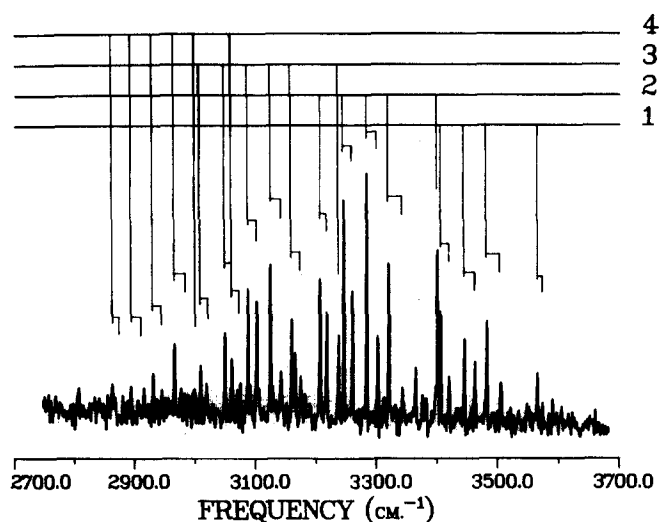


FIG. 1. $\Delta = -1$ OH emission spectrum obtained in the lowest-pressure experiment (#3, Table I). The upper vibrational states are indicated at the right. The frequencies of the P- and Q-branch transitions are shown by vertical lines; the $^2\Pi_{3/2}$ component of the spin doublet is at the left side in each case.

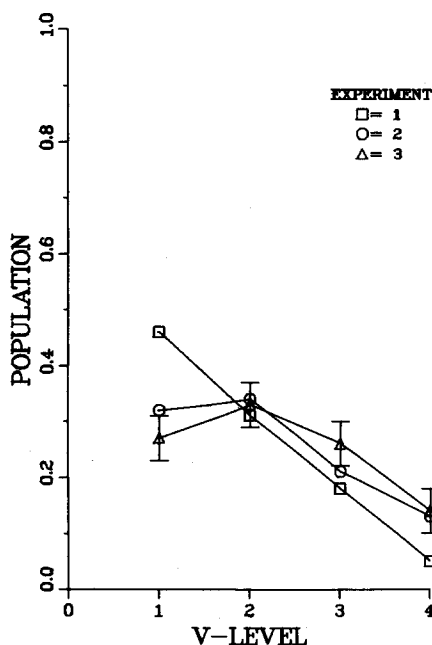


FIG. 2. OH vibrational population distributions measured in the experiments listed in Table I.

shown on the points for experiment 3 were estimated by measuring the rms noise amplitude, expressing this as a fraction of the average line intensity and normalizing the result to the same scale as the populations.

Several aspects of these distributions should be noted. First, it can be seen that a slight vibrational inversion, peaking in $OH(v' = 2)$ is observed. This inversion lies within the error bars estimated as indicated above. The precise value of the $v' = 2/v' = 1$ population ratio is not important, however. The significant result is that substantial OH vibrational excitation (greatly in excess of statistical) is produced by the reaction.

Comparing the results for experiments 2 and 3 shows that decreasing the ratio of CH_4/O_3 causes a slight increase in the observed product vibrational excitation. A similar increase (averaging a few percent per v' level) in the observed excitation results from decreasing the total reagent pressures, although in the latter case, the consequent degradation in signal to noise causes the small change to be less than the size of the error bars. This behavior is characteristic of experimental conditions in which the $OH(v')$ suffers a small amount of vibrational deactivation in collisions with unused reagent gases. Since collisional energy transfer cannot increase the vibrational excitation (*vide infra*), the data of run 3, Table I, represents a lower limit to the correct $OH(v')$ distribution. The size of the response to small changes in reagent concentrations indicates that this distribution differs by not more than a few percent per v' level from the initial distribution.

Emission from vibrationally excited CO (in the first two vibrational levels) was observed in the experiments done with the older reagent inlet and in certain experiments done with the variable inlet, including experiment 2 but not experiment 3. This is being explored in work presently under way.

Initial results suggest that this originates in the secondary reaction of a methyl radical with a reagent $O(^1D_2)$ atom. It is only observed in experiments done at higher pressures and cannot be seen in the experiments used to obtain the OH vibrational distribution reported here. Since the detectivity of our apparatus for CO is nearly three times that for OH, we conclude that no secondary reactions interfered with the determination of the OH vibrational distribution quoted here.

Using a numerical model of the system, we have calculated the time-dependent concentrations of the important species in the reaction in order to further demonstrate that the time scales imposed by the rates and the pumping speed ensure that no secondary processes can occur. Measured (literature) rate constants were used for all the reactions of interest. These are quoted in the following discussion with appropriate references. The residence time in the observation zone was obtained from the measured pumping speed. The partial pressures of CH_4 and O_3 were measured directly. The initial $O(^1D_2)$ reagent concentration was determined by assuming (on the basis of the O_3 photodissociation cross section¹⁹ and the laser pathlength) that 20% of the ozone is photolyzed in each laser pulse. The rate equations were numerically integrated using a fifth-order Runge-Kutta procedure.

The calculated time-dependent concentrations of $O(^1D_2)$ (O^*), CH_4 , and vibrationally excited OH (XOH) are shown in Fig. 3. The arrow labeled "C" indicates the average time between gas kinetic collisions. The only important processes removing $O(^1D_2)$ are reaction with CH_4 and (reactive) quenching by O_3 . The former rate is 4×10^{-10} ,^{6(a), 6(b), 6(c), 12, 20} the latter is 5×10^{-10} ,²¹ both in units of $cm^3 molecule^{-1} s^{-1}$. Since both of these are reactive processes and both rates are approximately gas kinetic (or slightly greater), the $O(^1D_2)$ reagent is removed from the reaction zone within approximately the first gas kinetic collision. This eliminates the possibility for later (secondary) reaction with the products of the primary reaction. It also ensures that the $O(^1D_2)$ reacts before it is translationally thermalized. Assuming that the fraction of the available energy partitioned into relative translation in the 248 nm photolysis of O_3 is the same as that for the 266 nm photolysis, the relative kinetic energy of the O

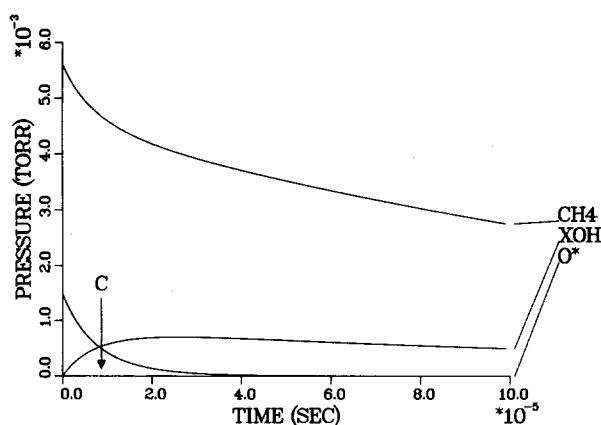


FIG. 3. Time dependence of the concentrations of CH_4 (CH_4), $O(^1D_2)$ (O^*), and total vibrationally excited OH (XOH) calculated using a numerical model of experiment 3, Table I. All rate constants are given in the text.

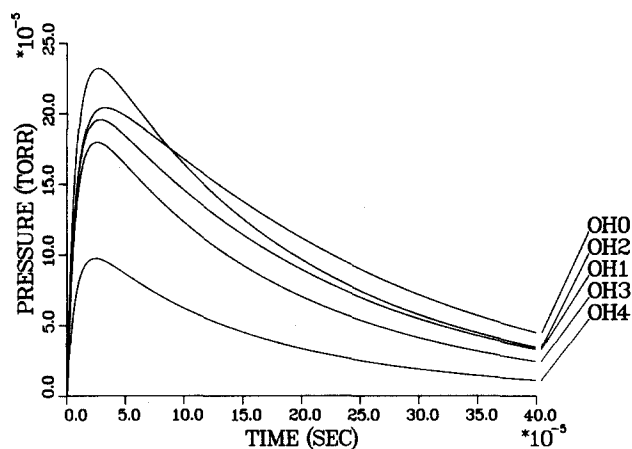


FIG. 4. Calculated time dependence of the concentrations of the individual OH vibrational levels under the conditions of experiment 3. Energy transfer rate constants are given in the text.

and O_2 is about 63 kJ mol^{-1} .²² Assuming a thermal translational distribution of CH_4 velocities, this results in a relative kinetic energy of about 23 kJ mol^{-1} in the $O(^1D_2)/CH_4$ collision. Therefore, the vibrational distributions reported in this work are produced in collisions having this (average) relative kinetic energy.

The evolution of the individual OH vibrational populations as a function of time were also calculated using the same numerical model in order to obtain a realistic estimate of the effect of vibrational deactivation on an assumed primary vibrational distribution. The absolute microscopic rate constants for $OH(v')$ formation were obtained from the distribution measured in experiment 3 and the total rate constant quoted above. For this purpose it was assumed that the rate into $OH(v' = 0)$ is the same as that into $OH(v' = 1)$. Only $\Delta v = -1$ deactivation processes were permitted, by analogy with the observed behavior of comparable HF systems.²³ The rate constants for deactivation of the lower vibrational levels were obtained by scaling absolute measurements for $OH(v' = 9)$ deactivation using the vibrational dependence reported in Ref. 24. The rate for removal of $OH(v' = 9)$ by CH_4 is 5×10^{-12} ²⁵ and that for removal by O_3 ²⁶ is 2×10^{-10} in units of $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

The time evolution of the vibrational populations is shown in Fig. 4. The partial pressures of the individual $OH(v')$ levels are indicated by OHV. The experiment as described in the previous section observes the time average of the populations, which is proportional to the integral under the individual curves. The observed temporal behavior of the total emission is well reproduced by the sum of these curves—that is, it reaches a maximum at 20–50 μs and decays about 500 μs after initiation of the reaction. Figure 4 shows that the shape of the assumed initial distribution persists (within a few percent) during the time the emission would be observable. In spite of the very high O_3/OH deactivation rate, the major removal of vibrationally excited species is still by pumping out of the observation zone. This provides further support for the observation, mentioned above, that the distributions measured by this technique are a close lower limit to the correct initial distributions.

IV. DISCUSSION

In previous work on this reaction,¹³ it was found that the rotational distributions in the $v' = 0$ and $v' = 1$ levels are strongly inverted and it was estimated that the total populations of these two vibrational levels are about equal. This estimate is consistent, within the signal to noise of both experiments, with a simple extrapolation of the results reported in the previous section of this work. The observed energy distributions in both of these product modes, therefore, demonstrate that the energy partitioning in the reaction between $O(^1D_2)$ and CH_4 is specific, as opposed to statistical.

It should be noted that the (LIF) experiment reported in Ref. 13 was carried out under a large excess of Ar buffer gas which was introduced in order to thermalize the reagent translational energy. As a result, the collision energy in that case was $3/2 kT$ or about 3.7 kJ/mol. As mentioned in the previous section, the reagent translational energy in the present experiments was about 23 kJ/mol because it was not possible to add buffer gas (due to limitations in the pumping capability). As a result of the different translational energy regimes sampled by the two experiments it is not clear that the two vibrational distributions ought to be the same, hence the above comparison of the vibrational distributions may not be appropriate.

In this context, it might be expected that both the cross section and the dynamics of this reaction would depend on the relative translational energy of the reagents. In previous work, the dynamics [by analogy with those of $O(^1D_2) + H_2$] have been interpreted in terms of a competition between direct hydrogen abstraction and complex formation via an insertion mechanism. Following this analogy, it may be assumed that there is a (small) barrier to abstraction, whereas that to insertion is negligible. In this case, the cross section for abstraction would increase with increasing translational energy but that for insertion would not (or would increase much more slowly). This model predicts that the reaction at high translational energy would shift towards more direct dynamics; the complex insertion component would become less important.

Certain aspects of the $O(^1D_2)/CH_4$ reaction dynamics may be modeled in terms of similar hydrogen abstraction reactions by fluorine atoms. The latter have the same mass combination and very similar exoergicities. In the F-atom reactions, the abstraction events produce much higher product vibrational excitation than those which form a long-lived intermediate complex [the analogy with $O(^1D_2)$ insertion]. Typical of the abstractions are the F atom reactions with hydrogen halides (see review, Ref. 27) which give strongly inverted HF. Long-lived complex formation, on the other hand, cannot produce total inversion and in most cases gives very cold HF vibrational distributions.¹⁷ In terms of this model, the distribution recorded in the present work for the $O(^1D_2)/CH_4$ reaction is much closer to the result expected from an abstraction than from an insertion.

In these comparisons, caution must be exercised when drawing conclusions about higher polyatomic reactions based on triatomic observations. Apart from the obvious differences in such aspects as barrier heights, there are qualitative differences resulting from the fact that the potential sur-

face experienced by the oxygen atom during a perpendicular approach to the C-H bond is much more complicated than for approach to an H₂ bond. Additionally, the CH₄ reaction has the possibility for the insertion-elimination channel leading to CH₃O + H and it is certain that many of the insertion events would proceed via this channel. Since this channel is not available to the triatomic reaction, the observed OH distributions would also be influenced by this effect.

V. CONCLUSION

The reaction between translationally excited O(¹D₂) and CH₄ produces OH with substantial vibrational excitation. A slight inversion is observed in the $v' = 2/v' = 1$ population ratio, but a broad range of vibrational states are populated, including the maximum-allowed level, $v' = 4$. In subsequent work on this reaction, it is hoped that the dependence of the vibrational distribution on the reagent translational energy may be explored.

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