ENERGY PARTITIONING IN THE REACTION $O(^1D) + H_2O \rightarrow OH + OH$

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The rotation–vibration population distribution of nascent OH formed by the exothermic reaction $O(^1D) + H_2O \rightarrow$ OH + OH has been observed by means of time-resolved resonance absorption using a pulsed laser with sub-Doppler linewidth. The translational energy of most of the product molecules is distributed according to a temperature of about 4800 K. One half of the OH is found in a rotational distribution described by $T \approx 400$ K, whereas the other half is rotationally hot (1900 K). The vibrational distribution is extremely non-thermal. The populations in the two different spin states $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ are statistical, but non-statistical in the corresponding Λ components.

Hydroxyl radicals are important reactants in ordinary chemistry as well as in atmospheric chemistry. In the earth's atmosphere they are products of the photochemical activity of the sun [1]. They also exist in interstellar clouds and are the origin of strong 18 cm radiation [2].

Recently we studied the reaction

$$O(^1D) + H_2O \rightarrow OH + OH ,$$
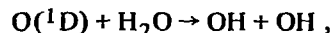
which is an excellent example for the study of the dynamics of a chemical reaction [3]. Nanosecond laser spectroscopy allows the investigation of the complete energy partitioning in this reaction. It was observed that the exothermic reaction forms OH radicals which exhibit population inversion in the lower and anti-inversion in the upper Λ states. But not only inversion or anti-inversion in the Λ states was observed; such phenomena also appeared for the different hyperfine states. Despite the fact that the partitioning of excitation energy of OH in the lower rotational states follows to some extent a temperature distribution, these effects are strongly non-thermal. New measurements were carried out covering the higher rotational states of $v'' = 0$ up to $K = 18$ and also rotational states of $v'' = 1$. Due to the fact that the laser linewidth is sub-Doppler, the kinetic energy of the product molecules could be determined. The variation in the delay time between the photolysis and monitor beam made

it possible to observe rotational as well as translational relaxation.

The apparatus is identical with that described earlier [3]. The fourth harmonic of a Nd:YAG laser at 266 nm is used to photolyse ozone and to produce $O(^1D)$. The gas flowing through the reaction cell is a mixture of ozone (2 Torr) and water (10 Torr) at a total pressure of 12 Torr. Part of the second harmonic of the Nd:YAG laser pumps a dye laser which is pressure-tuned and frequency-doubled to monitor the OH molecules by absorption of resonance radiation. As the $O(^1D)$ need a certain time to react with H_2O, that part of the second harmonic which pumps the dye is optically delayed. Such a delay by multiple reflection of the beam provides a jitter-free operation. The observation of the absorption instead of resonance fluorescence makes the original ground-state population directly observable.

Most of the experiments were carried out at 10 ns delay time while others were done at somewhat different conditions, e.g. 20 or 60 ns delay time or at total pressures reduced to 3 Torr. This was necessary to study the influence of relaxation upon the partitioning of internal and external energy among the products.

The complete set of reactions describing the production of OH is given by

$$O_3 + h\nu \ (266 \text{ nm}) \rightarrow O(^1D) + O_2(^1\Delta_g) , \qquad (1)$$

$$O(^1D) + H_2O \rightarrow OH + OH . \tag{2}$$
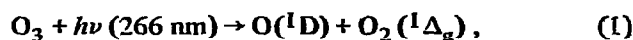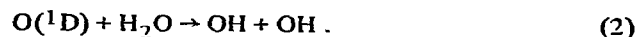
As the quantum efficiency of (1) has recently been established to be nearly 0.9 [4] the number of OH radicals formed by (2) can be calculated from the laser energy density, the known gas concentrations, and the rate constant of (2) [5].

At room temperature the Doppler width of the resonance transition $X\ ^2\Pi(v'',J'') \rightarrow A\ ^2\Sigma^+ (v',J')$ is about 3 GHz. With the laser linewidth kept at about 1 5 GHz translational energies can be determined under the assumption of a statistical distribution of particle velocities.

Recently we gave a preliminary report on the distribution of OH radicals from reaction (2) in rotational levels $K > 6$ of $v'' = 0$ [6]. Two quite different distributions were observed with 50% of all OH formed by (2) being distributed according to $T \approx 400$ K while another 25% of the OH could be described according to $T \approx 1900$ K. These measurements are now much extended and improved results on the population N_J in the rotational levels of $v'' = 0$ and also of $v'' = 1$ obtained. Results are presented in fig. 1 for the spin systems $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ for the upper Λ levels of $v'' = 0$.

We see from fig. 1 that a sharp break in the population of the rotational levels exists at $K = 6$. The values are given for the upper Λ levels, both in $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$. Similar results were also obtained for the lower Λ levels The experimental points for the two spin systems fall on the same straight line, demonstrating that the particles are distributed statistically among the two spin systems. But the distribution of the two corresponding Λ-doublet components is non-statistical.
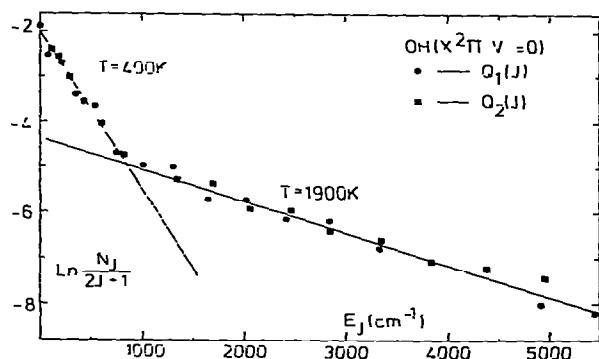
The lower levels are always more populated than the corresponding upper ones. The ratio of the average population densities is 1 3. Deviations from this average value exist and are found to be systematic, showing that the parity of the states evidently influences these ratios. The results will be discussed in a forthcoming paper [7].

If the experiments are extended to rotational states in the first vibrational state of OH, a very similar distribution is obtained (fig. 2). Again the rotational state population is described by a temperature T of nearly 1900 K. In this case R transitions were registered which is a probe for the lower Λ components. An interesting result in this context is the non-uniform distribution of the rotational population. It is evident that for low rotational quantum numbers a small number of molecules is already in a relaxed distribution. These molecules amount to less than 1/4 of the total population in this vibrational state As demonstrated later, the larger part of the total available energy of this reaction is released in the translational mode producing translationally hot molecules. These molecules have larger velocities than those of the ambient gas and therefore experience shorter collision times. This influence can readily be observed by reducing the total gas densities to 1/4 of that at normal conditions.

From their kinetic energies we calculate that on the average each OH molecule suffers one collision before it is monitored. The collision number can be slightly lower in the case of the $v'' = 1$ molecules compared to $v'' = 0$ because their kinetic energy is lower from con-
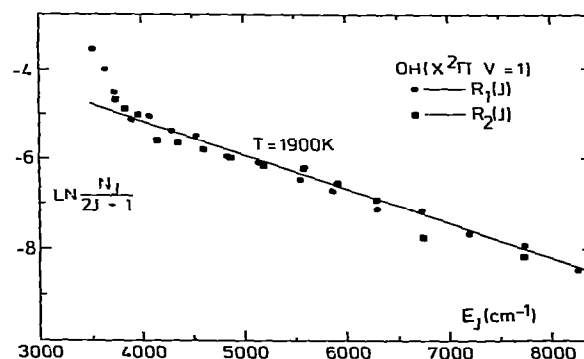

Fig. 1. Distribution of product OH in rotational states of $^2\Pi_{3,1/2}$ ($v'' = 0$) for the upper Λ levels.

Fig. 2 Distribution of product OH in rotational states of $^2\Pi_{3/2,1/2}$ ($v'' = 1$) for the lower Λ levels.

servation of energy. We therefore expect a somewhat larger part of the OH to be found in a relaxed distribution for the $v'' = 0$ molecules. Due to the high percentage of OH observed in $v'' = 0$, we think that this relaxation accounts only partly for the measured distribution.

From the absorption measurements we can calculate absolute populations. As 70% of all OH formed by (2) has been observed in $v'' = 0$, there is 30% left which is distributed in higher vibrational states. If we add up the number densities of OH in the two states $v'' = 0$ and $v'' = 1$, we find that the number of OH molecules excited in the $v'' = 1$ state amounts to about 20% of the total OH. We therefore expect 10% of the OH formed by (2) to be excited in $v'' \geqslant 2$, as the total available energy is high enough to excite OH up to $v'' = 3$.

Following the interpretation that the OH with the "old" bond (already preformed in H_2O), amounting to 50% of total OH, is in $v'' = 0$ (cold OH), we can proceed to calculate the distribution of the OH with the "new" bond (hot OH). This distribution is shown in fig. 3. Fig. 3 contains an extrapolation for the higher vibrational states. It shows that the vibrational states $v'' = 0$ and $v'' = 1$ of OH in the newly formed bond are nearly equally populated, indicating that a strong non-thermal distribution exists ($N_{v''=1}/N_{v''=0} \approx 1.0$).

An important point in the discussion of the dynamics of the reaction is concerned with the translational energy of the products. It should be mentioned that the absorption intensities were taken from the integral of an absorption line, considering not only the peak
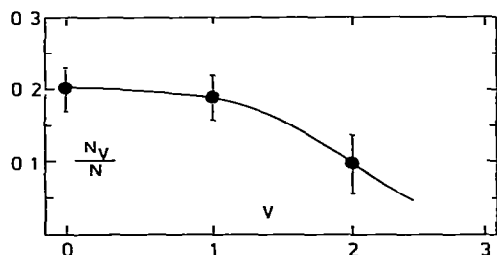
height but also the linewidth. From these measurements, it follows that the absorption lines are much broader than the corresponding width of room-temperature molecules. The measurements made at 12, 6 and 3 Torr, show that the widths of the absorption lines change with pressure. An extrapolation of these values to zero pressure, taking into account the reduction in particle velocity, leads to $\Delta\nu_{fwhm} = 12$ GHz, which is four times the width at 300 K (table 1). As the Doppler width is proportional to the square-root of the temperature, this corresponds to a temperature of nearly 4800 K, which is somewhat more than twice the temperature found for the rotational distribution of hot OH.

For the atom–molecule reaction, the distribution of product energy states will be specified in terms of the partitioning of total available energy (E) between the translational (E_T), vibrational (E_V), and rotational (E_R) modes, where

$$E = E_T + E_V + E_R .$$

It is practical to consider the fraction of energy in a specific mode, $f_s = E_s/E$ where s = T, V, R with

$$f_T + f_V + f_R = 1.$$

The total available energy, $E \approx 37$ kcal/mole, is determined by the excitation and translational energy of the oxygen atoms, which can be calculated from results of Sparks et al. [4], by the thermal energy of H_2O, and by the exothermicity of the reaction. From the measured distributions of the products in the different vibrational and rotational states, and from the determination of their translational energy, it follows that $f_T = 0.57$ in the minimum.

About 60% of the total energy release is in the translational degrees of freedom. f_R for the rotational state distribution is at most 0.21, leaving about 20%

Fig 3 Distribution of the hot OH product molecules in vibrational states of $^2\Pi_{3/2,1/2}$ related to a total production of two OH molecules (N) in reaction (2).

Table 1
Width of OH absorption line Q_2 (4) at various pressures in the reaction cell (delay time 10 ns)

P (Torr)	$\Delta\nu_D$ (GHz)
3	3.5
4	3.3
6	2.9
12	2.3

of E stored in the vibrational modes of the OH molecules ($E_V \approx 8.2$ kcal/mole). From $N_{v''=1}/N_{v''=0} \approx 1.0$ and $T \approx 1900$ K for the rotational distribution in $v'' = 1$, a contribution of 4.2 kcal/mole to E_V is calculated. This leaves only 4.0 kcal/mole or 11% of the total available energy for the excitation in vibrational states $v'' \geqslant 2$. As these particles amount to roughly 10% of the OH product molecules a minimum contribution of about 4 kcal/mole to E has to be considered. As the translational energy is a quadratic function of the linewidth (which is the experimental parameter) an error of only 5% of this value amounts already to a 10% error in the translational energy. According to the large value of f_T, an experimental error of 5% results in 2 kcal/mole.

The four-fold decrease in total pressure from 12 to 3 Torr leads to a considerable reduction in the collision frequency. Using a simple collision model (collision cross section for $OH-H_2O$ collisions independent of particle velocity in the range of interest) the percentage of OH having suffered one collision is less than 20%. However, translational relaxation is quite effective (table 1) because in this experiment the main collision partner of OH is H_2O, a particle of nearly equal mass.

The observation that about 70% of the reaction products are in the vibrationless ground state leads to the question to what extent the old bond contributes to this distribution. An easy proof can be made by substitution of ^{16}O in H_2O by ^{18}O. In this case the reaction products are different the newly formed OH contains the light oxygen isotope whereas ^{18}O is present in the old OH bond.

Preliminary results show that ^{18}OH is the main constituent of the $v'' = 0$ molecules whereas ^{16}OH is by far the most abundant constituent in the $v'' = 1$ distribution [7].

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