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ENERGY PARTITIONING IN THE REACTION $O(^1D) + H_2O \rightarrow OH + OH$.
V. ROTATIONAL RELAXATION OF $OH(X\,^2\Pi, v'', J'')$

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The rotational relaxation of $OH(X\,^2\Pi, v'', J'')$ in $v'' = 0$, 1, and 2 produced from the reaction of $O(^1D)$ with H_2O has been studied as a function of H_2O vapor pressure and added argon. Water molecules are extremely efficient in bringing about relaxation and the experiments performed indicate that, on the average, the high temperature distribution is relaxed to nearly room temperature at a gas kinetic rate. This observation is rationalized by assuming a collision complex between OH and H_2O having a quasichemical interaction similar to weak hydrogen bonding. The nascent OH internal energy distribution does not depend upon the translational energy of the $O(^1D)$ reactant. Translational relaxation of the nascent OH product by H_2O is fast, as fast as rotational relaxation.

1. Introduction

The reaction of metastable oxygen atoms in the (^1D) state with water molecules leads to two OH product molecules. The spectrum of OH [1,2] is simple and fully resolvable with present-day spectroscopic instruments so that very detailed information on energy partitioning for this important reaction can be obtained [3–7]. These details involve energy which is partitioned not only into rotational and vibrational excitation of the product molecules, but also into fine and even the hyperfine states. Therefore, the influence of the electron and the nuclear spin on the distribution of the excess energy among the products can be considered. Such results are exceedingly important for a discussion of the dynamics of the reaction.

It is evident from the experiments that we are dealing here with a direct type of chemical reaction instead of a reaction via a complex [4,5]. The two OH product molecules can be clearly classified into one which originates from the old bond in the water molecule and the other which is newly formed with the atomic oxygen reactant. In addition, information theory allows us to discuss much finer details of the reaction mechanism. One such details is the microscopic probability of forming coincident pairs of OH product molecules [8]; in other words, if one OH molecule is formed in a specific (v'', J'') state a prediction can be made in which (v'', J'') state the second OH will be simultaneously formed. Analysis of this kind has been carried out for the first time using the above reaction as an example [8].

To obtain such detailed information from the experimental data, it is necessary to observe the OH product molecules in their nascent distribution, i.e., under collision-free conditions. This can be performed either by a molecular beam type experiment or by applying a fast production–detection cycle, which is provided by nanosecond spectroscopy. The latter procedure is preferable if the reaction is fast, and offers a further advantage because the experiments are generally carried out under higher particle densities compared to molecular beam experiments. This results in a higher sensitivity so that relatively weak populations can still be observed.

Consideration of the reaction

$$O(^1D) + H_2O \rightarrow OH + OH + \Delta E\,, \qquad (1)$$

has demonstrated that the OH product molecules lose their rotational excitation very efficiently in collisions. Therefore experiments have been carried out to

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study this effect in more detail. The experimental results show that the water molecule is the most efficient collision partner in the system. The observed relaxation effect is of special interest in the study of chemical reactions in which OH molecules participate, because the OH internal energy may accelerate these reactions. Another field for which the knowledge of the internal state distribution of the OH and its relaxation in collisions is of great importance is atmospheric chemistry. The detection of atmospheric OH in ambient air by laser-induced fluorescence is strongly dependent on any processes which populate or depopulate the monitored rotational states of OH [9–11]. Therefore, reliable values for the atmospheric OH concentrations cannot be obtained without knowledge of the relaxation effect.

2. Experimental

The experimental setup has been described in a previous paper [5]. We use a *Q*-switched Nd-Yag pumped dye laser to carry out the experiments. The laser light is frequency doubled (532 nm) and quadrupled (266 nm); pulse length $\Delta t = 6$ ns. The 266 nm UV flash is used for the photolysis of ozone, which flows through the reaction chamber together with water vapor. The partial pressure of ozone is held constant at 1.5 Torr, while the partial pressure of water vapor is varied between 2.5 and 17 Torr. The $O(^1D)$ atoms produced by the 266 nm radiation react with water vapor as in eq. (1), producing OH molecules. The range of pressures employed in the present study leads to reaction times (1/e times) between 8 and 40 ns [12].

The product OH molecules are observed through their absorption of resonance radiation ($A\,^2\Sigma \leftarrow X\,^2\Pi$) around 308 nm, which is provided by the dye laser. In order to allow the $O(^1D)$ atoms an opportunity to form OH molecules by reaction with H_2O, the UV pulse of the narrow bandwidth frequency-doubled dye laser ($\Delta\nu = 1.5$ GHz, $\Delta t \approx 5$ ns) is delayed by 10 ns relative to the photolysis flash. (The room temperature doppler width of an OH absorption line is 3 GHz.) By utilizing the known transition probabilities [13,14], the absolute concentration of OH molecules can be determined from the strength of their absorption. The determination of the OH product molecule concentration by means of the resonance fluorescence technique, which is in general more sensitive, is not advisable in this case because the corresponding upper electronic state of OH($A\,^2\Sigma^+$) is rather long lived. This causes the excited OH molecules to undergo efficient quenching collisions especially when performing relaxation measurements at elevated pressures. Instead the absorption technique permits the OH ground state population to be determined directly. There is, however, a further advantage of the absorption method in that it allows monitoring the OH product molecules in vibrational states $v'' > 1$. Such measurements are very difficult, if not impossible, using the fluorescence method due to predissociation of corresponding states of OH($A\,^2\Sigma^+$) [15,16].

The study of the rotational relaxation phenomenon has been performed by observing the OH product state distribution at different water vapor pressures leaving the ozone partial pressure constant. In order to discriminate against the very efficient relaxation by the water molecules, experiments with argon as atomic collision partner were also carried out. Pressures of argon used were up to 40 Torr ($[Ar] : [H_2O] = 8 : 1$).

3. Results

The measurements on the efficiency of OH rotational relaxation were carried out under four different experimental conditions. The most careful studies were made with only rotationally excited OH($^2\Pi$, $v'' = 0, J''$). Collision partners were water molecules in one case and argon atoms in the other. Further experiments were carried out with vibrationally excited OH($^2\Pi, v'' = 1, J''$) and OH($^2\Pi, v'' = 2, J''$). In the latter two cases the influence of water vapor alone on the relaxation was studied. Due to the fairly low OH populations in these vibrational states only an order of magnitude of the effect was calculated from the measurements. In no case was specific consideration given to the effect of different electron spin or hyperfine states; instead only arithmetic means were taken so that the pure rotational effects were extracted.

The addition of an atomic collision partner, e.g. argon, to the reaction mixture composed of ozone and water vapor can cause, in principle, two different relaxation effects. It influences the translational energy of the reactants and products, and it may change the internal state distribution of the energetic OH products. The effect on the translational energy of the O(^{1}D) reactants [17] is very important because the translational cooling decreases the total energy available in the reaction [8]. From a recent observation we know that the reaction rate is not influenced by the translational energy of the O(^{1}D) [12]; but the question remains whether the energy distribution between the product molecules will also be independent of the O(^{1}D) translational energy.

The answer can be seen from fig. 1. The diagram contains the rotational state distribution of OH in its ($^2\Pi$, v'' = 0) state with and without the addition of 40 Torr argon. The two different curves represent the results of the $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ spin states, respectively. Ozone and water vapor were kept at 1.5 Torr and 5 Torr, respectively, throughout the experimental series. The figure shows no detectable effect from the O(^{1}D) kinetic energy, thus the translational energy of the O(^{1}D) does not influence the nascent OH rotational state distribution. An estimate of the change in kinetic energy of O(^{1}D) can be made from an earlier observation [12]. In the case of added argon the kinetic energy of nascent O(^{1}D) from the photodissociation of O_3 at 266 nm is roughly 1/3 of the original kinetic energy (that is, about 1.5 kcal/mole).

The results of fig. 1 contain further important information. As the argon atoms also undergo collisions with the OH product molecules the influence of such collisions on the rotational state distribution can be observed. For a delay time of 10 ns, we observe no effect, which means that the rotational relaxation of OH($^2\Pi$, v'' = 0, J'') in collisions with argon is not very efficient. We estimate from these results that considerably more than 10 collisions are needed to relax the OH rotations. With this background we can now proceed to study the rotational relaxation of OH with water vapor alone. The results are shown in fig. 2 in the form of a logarithmic plot, of $\ln(N_J/2J+1)$ versus the rotational energy E_J. We see that the data points closely approximate the solid curve, which itself is a sum of the two indicated straight lines. Each of these lines represents a Boltzmann rotational distribution, the slope is inversely proportional to the temperature of the distribution. The analysis of the data points leads to the conclusion that the experimental results can be interpreted in terms of two different temperatures. Table 1 summarizes such an analysis showing not only the two different temperatures for a number of partial pressures of water vapor but also the percentage N_L/N of the particle number den-

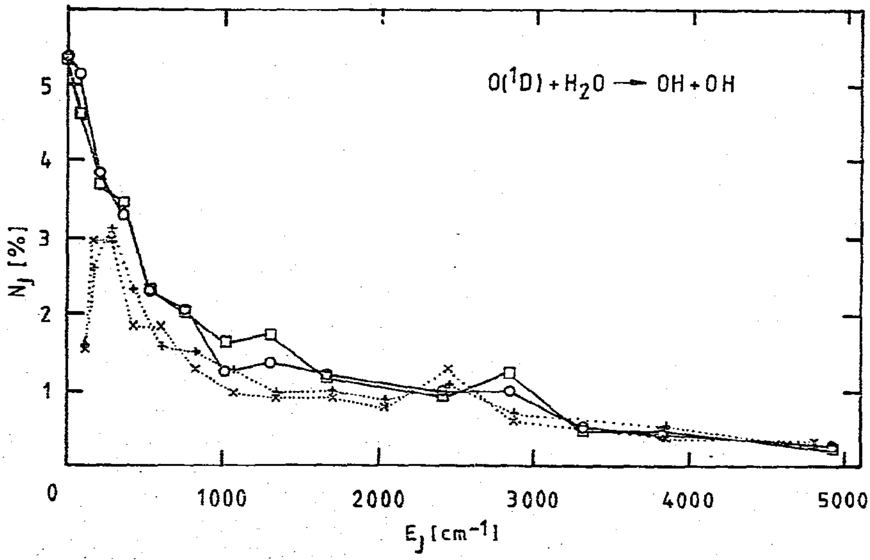

Fig. 1. Influence of argon buffer gas on the rotational distribution of OH product molecules (concentration of OH versus rotational energy E_J). □: OH($^2\Pi_{3/2}$, v'' = 0); ○: with 40 Torr argon added; +: OH($^2\Pi_{1/2}$, v'' = 0); X: with 40 Torr argon added.

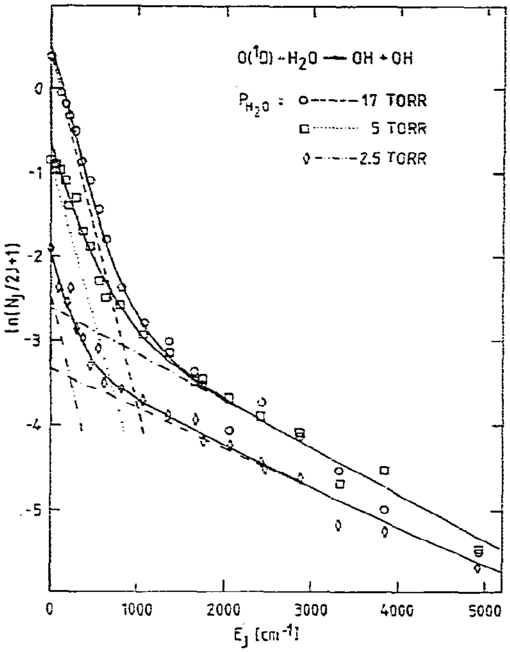

Fig. 2. Rotational distribution of OH product molecules at different water vapor pressures [$\ln(N_J/2J+1)$ versus E_J].

sities belonging to this low temperature distribution. We see from this table, and also from fig. 2, that the number of OH radicals belonging to the low temperature distributions increases rapidly with added water vapor pressure (see also fig. 3).

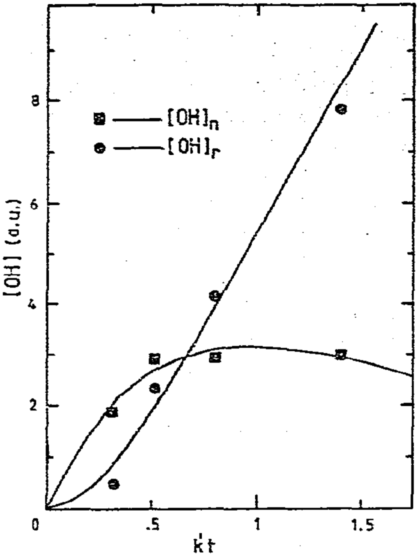

Fig. 3. Concentration of OH molecules in the relaxed, $[OH]_r$, and the nascent distribution, $[OH]_n$, as function of $k't$. $k' = k[H_2O]$; delay time t was always kept at 1×10^{-8} s.

Whereas most of the experiments were carried out without isotopically labelling the oxygen in the water molecule some were performed with $H_2\,^{18}O$. Also the individual distributions of ^{16}OH and ^{18}OH show the same appearance as already discussed: they are represented by two different temperatures [4,5]. If we now proceed in the same way as already performed in the non-labelled case, namely taking the ratio of the particle densities belonging to these two different distributions then we obtain $N_L/N = 0.43$ for ^{16}OH and $N_L/N = 0.55$ for ^{18}OH, with both molecules in the $(^2\Pi, v'' = 0)$ state. From these two values one might conclude that the two isotopic species behave differently. This is not the case. We have to consider that in each reactive collisions two OH radicals are formed simultaneously. From our earlier experiments we know, however, that nearly 18% of the ^{16}OH formed is in $v'' = 2$. From energy conservation and rotational constraints the counterpart of these $^{16}OH(^2\Pi, v'' = 2, J'')$, that is, the coincidentally produced ^{18}OH, must be in the vibrationless state $v'' = 0$. This fraction is superimposed on the low temperature distribution – it does not originate from a relaxation process. We therefore have to subtract 20% from the number density of the low temperature distribution of ^{18}OH in order to correct for this effect, giving a ratio of 0.44. This is in

Table 1
Temperature parameter of the nascent and the relaxed rotational distribution as a function of water vapor pressure. N_r/N is the fraction of particles in the relaxed distribution

P_{H_2O} (Torr)	T_r (K)	T_n (K)	$N_L/N = N_r/N$
2.5	320	3000	0.18
5.0	390	2600	0.44
10.0	320	3000	0.60
17.0	350	2700	0.72
5.0 +40 argon	350	3000	0.5

excellent agreement with the results for ^{16}OH, showing that there is no molecular exchange going on in the collision process.

For vibrationally excited OH with quantum numbers $v'' = 1$ and $v'' = 2$ the measurements were carried out only at one partial pressure of water vapor (p_{H_2O} = 10 Torr) and without isotopically labelling the water. Therefore only an order of magnitude of the effect shall be given. The observed ratio, N_L/N_H, in the case of OH($^2\Pi$, $v'' = 1$, J'') is ≈0.4. This is somewhat less than was found for OH in the vibrationless state $v'' = 0$. In the latter case the sum over ^{16}OH and ^{18}OH would lead to a ratio of ≈0.5 (see table 1). The experimental results, therefore, reveal that rotational relaxation of OH($^2\Pi$, $v'' = 1$, J'') in collisions with water molecules shows a tendency to be less effective than in the corresponding case with OH in ($^2\Pi$, $v'' = 0$, J'').

In the case of OH($^2\Pi$, $v'' = 2$, J'') only an estimate can be made. First, the total amount of OH in this vibrational state is low, being less than 10% of the overall population. Second, the rotational temperature distribution of nascent OH in this state (600 K) is not far from the expected relaxed distribution (≈300–400 K). Yet the results indicate that no more than 10–20% of the OH is in the low temperature distribution under the experimental conditions. This means that the previously observed tendency towards a decrease in the efficiency of rotational relaxation with vibrational excitation continues to hold.

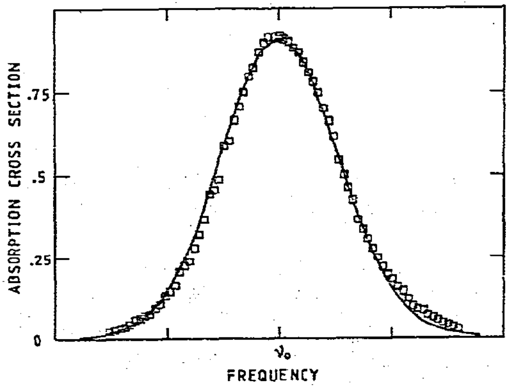

Fig. 4. Shape of $Q_1(5)$ OH absorption line (□ data points). Solid line: Doppler profile (best fit).

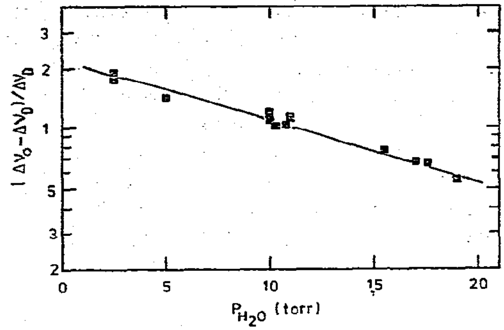

Fig. 5. Change of width of $Q_1(5)$ OH absorption line with water vapor pressure. The ordinate scale is the logarithm of the difference in the line widths between the observed line ($\Delta\nu_0$) and the calculated Doppler line at equilibrium ($\Delta\nu_{eq}$).

The total energy release in the reaction (1) is in the rotational, vibrational, and translational modes of the OH products. As was already explained in section 2, a narrow bandwidth laser was used to monitor the OH molecules, which permits observing the absorption line shape and its width. Generally this is the Doppler width so that this type of measurement provides us with the average velocity of the OH product molecules. Fig. 4 shows such an example for the absorption line $Q_1(5)$. This line has a lineshape which is gaussian to a high degree of accuracy (deviation ≈1%).

Measurements at different partial pressures of water vapor were made with results given in fig. 5. In this figure the difference between the observed line width and the equivalent Doppler width at room temperature (300 K) is drawn versus the H_2O partial pressure, showing a nearly linear decrease on a logarithmic scale. These linewidths always contain the integrated information over all OH within the 10 ns observation time and therefore give a lower limit for the relaxation effect. From the first order decay (fig. 5) we calculate an average value for the rate constant of translational relaxation to be $> 2.3 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}.

4. Discussion

The ideal experiment for studying rotational relaxation is a state-to-state experiment, in which we are able to measure specific rates of collisional transfer from one rotational quantum state to another. In the experiment to be discussed here this is not fully possible because the molecules to be studied are not prepared in a single isolated state but are spread over a distribution as a result of chemical reaction.

A number of approaches have been developed to describe rotational relaxation. The exact way is to start with the Schrödinger equation, compute the potential energy surface, and then apply exact quantum mechanical methods to solve for the scattering cross sections. In our five-centre problem this procedure will certainly not be feasible. In a problem like the above we are faced with the situation that while OH radicals are continually being formed in a state distribution by the chemical reaction, relaxation processes occur simultaneously. Although the population in the individual rotational levels is always observed at the same time *t* after the initiating photolysis pulse, the time scale of the reaction, and also that of the relaxation, changes due to the change in reactant concentration. In this case a treatment of energy transfer involving many coupled levels is necessary.

The change of population in a state *i* due to the described processes is given by the differential equations

$$\mathrm{d}[\mathrm{OH}(i)]/\mathrm{d}t = \sum_f k_{fi}[\mathrm{H_2O}][\mathrm{OH}(f)]$$

$$- \sum_f k_{if}[\mathrm{H_2O}]\,[\mathrm{OH}(i)] + k_{ri}[\mathrm{H_2O}]\,[\mathrm{O}(^1\mathrm{D})], \quad (2)$$

containing the gain process not only from energy transfer but also from production through chemical reaction (k_{ri}). An additional term, i.e., a sink term due to subsequent chemical reaction of OH, need not be included because such processes occur on a time scale not relevant in this experiment.

Eq. (2) is called a master equation, which is a kinetic description of the time-dependent processes which lead to equilibrium. The equation can be simplified by introducing a *total* rate constant replacing the individual ones,

$$k_i = \sum_f k_{if}\,,$$

and by using the known individual rate constants of the chemical reaction. In the above case a whole set of such equations has to be used, one for each of the initial rotational levels ($i = 1, 2, ...$). The sum over all quantum states *i* (2) yields:

$$\sum_i \frac{\mathrm{d}[\mathrm{OH}(i)]}{\mathrm{d}t} = \sum_i k_{ri}[\mathrm{H_2O}]\,[\mathrm{O}(^1\mathrm{D})]\,. \quad (3)$$

The total number of OH radicals ($[\mathrm{OH}] = \Sigma_i[\mathrm{OH}(i)]$) formed in the reaction is given by:

$$[\mathrm{OH}] = 2k\,[\mathrm{H_2O}] \int [\mathrm{O}(^1\mathrm{D})]\,\mathrm{d}t\,. \quad (4)$$

This equation can be used to determine the rate constant *k* for the production of the OH radicals [12].

The experimental results show that the observed product distribution is fully described by two temperatures. If a least-squares procedure is carried out to fit the experimental results of fig. 2 to the sum of two temperature distributions, the results of table 1 are obtained. We see that within the 10–15% error of the experimental data for each partial pressure of water vapor the rotational distribution of the OH molecules can always be described by the same two temperatures, one giving the low temperature distribution, the other one the high temperature distribution. The relaxation effect is demonstrated by the ratios, N_L/N given in column 4. These ratios strongly suggest that, in a first order assumption, the relaxation effect can be described by a conversion of the high temperature (nascent) distribution as a whole into the low (relaxed) one. Following this idea for the rotational relaxation process, the phenomenon appears to be describable by introducing a single rate equaiton with the appropriate relaxation rate coefficient.

Before doing this we wish to examine more closely the nature of the nascent distribution‡. We see from table 1 that the ratio of N_L/N strongly increases with water vapor pressure. It remains to be determined whether the nascent distribution is only represented by the high temperature distribution or in addition by some part of the low temperature one. This assumption can be tested by solving the kinetic problem under the above mentioned simplifying assumption. Let us subdivide the nascent distribution, $\mathrm{OH_n}$,

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‡ The actual rotational energy distribution of $\mathrm{OH}(v'' = 0)$ is composed of several temperature distributions, as the recent results of a detailed theoretical treatment [8] of the problem has shown. But the different temperature distributions prove to sum up quite well to the observed distribution, so that the present approach offers a very good representation of the nascent rotational energy distribution by only one temperature parameter.

into two distributions: one, OH_{T_n}, at high temperature and one, OH_{T_r}, at the low temperature T_r, which is also the temperature of the relaxed distribution, OH_r. Then the following equations hold:

$$O(^1D) + H_2O \xrightarrow{k} 2(a\,OH_{T_n} + b\,OH_{T_r}) , \qquad (5)$$

$$a + b = 1 ,$$

$$OH_{T_n} + H_2O \xrightarrow{k_r} OH_{T_r} + H_2O . \qquad (6)$$

The next step is to calculate from the data of table 1 the ratios of the population numbers of the low temperature distribution to those of total OH as a function of added H_2O partial pressure. According to our simplifying assumption the relaxed distribution has to develop exponentially, which follows from the first order law (water vapor in excess). Fitting the data to an exponential expression, we find that the nascent distribution, (OH_n), is well represented by OH_{T_n} alone and that OH_{T_r} is solely the relaxed distribution, (OH_r) ($b \approx 0$). Eq. (6) describes rotational relaxation for any particular v'', excluding vibrational relaxation.

With this information we will now proceed to extrapolate a rate constant for the relaxation process under our simplifying assumption, considering only downward collisions:

$$\begin{aligned} d[OH_n]/dt &= k'[O(^1D)] - k_r'[OH_n] , \\ d[OH_r]/dt &= k_r'[OH_n] , \end{aligned} \qquad (7)$$

with k' and k_r' representing $k\,[H_2O]$ and $k_r[H_2O]$ respectively. It follows that

$$[OH_n] \approx \frac{k'}{k' - k_r'} (e^{-k_r't} - e^{-k't}) , \qquad (8)$$

$$[OH_r] \approx \frac{k'}{k' - k_r'} (1 - e^{-k_r't}) - \frac{k_r'}{k'} (1 - e^{-k't}) . \qquad (9)$$

Introducing $k_r' = ck'$ we get

$$[OH_n] \approx \frac{1}{c-1}\, e^{-k't}(1 - e^{-(c-1)k't}) , \qquad (10)$$

$$[OH_r] \approx \frac{1}{1-c}(1 - e^{-ck't}) - c(1 - e^{-k't}) . \qquad (11)$$

From the recently determined value for k [12] and the best fit to the experimental data it follows that

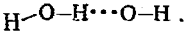
$$c = 1.1 \pm 0.1 .$$

With $k = 2.0 \times 10^{-10}\ cm^{-3}\ s^{-1}$ we obtain:

$$k_r = (2.2 \pm 0.5) \times 10^{-10}\ cm^{-3}\ s^{-1} .$$

The results of these calculations are twofold: the nascent rotational distribution of OH product molecules from reaction (1) is well described by a single (high temperature) Boltzmann distribution, and the use of a single rate equation for the rotational relaxation is a meaningful procedure, showing that the OH molecules relax with gas kinetic probability in collisions with water molecules.

The observation that the relaxation of OH by H_2O occurs at gas kinetic rates appears probably attributable to specific chemical interactions. Since OH and H_2O are likely candidates for hydrogen bond formation, "sticky" collisions persisting over several rotational periods might be expected. Such prolonged life of the collision complex would facilitate randomization of the energy of the OH radicals



The strongest hydrogen bond would be the one between a hydrogen atom of water and the oxygen of OH, with a bond energy of about ≈7 kcal/mole. The other type of bond, between the hydrogen of OH and the oxygen of water, is estimated to be not stronger than 3 kcal/mole. The expected bond length of the preferred bond will be nearly 1.8 Å corresponding to a distance between the two O atoms in the system of 2.7 Å.

Due to the long range of hydrogen bonding an early capture of the OH is possible. The opportunity for the colliding OH to transfer energy into the rotational mode of H_2O is therefore high. If enough energy is transferred from the OH to the water molecule, the OH will be captured and a randomization of energy can proceed. The complex will redissociate when the energy is stored in rotation about the center of gravity, so that centrifugal forces will cause the hydrogen bond to break.

A system such as the one described can be thought of as having seven rotational degrees of freedom: two for OH, three for H_2O, and another two for the floppy bond between the two collision partners. Equipartitioning of rotational energy among these degrees of freedom would transfer only 2/7 of this energy into the OH rotation, leading to an OH rotational temperature of about 700 K if the energy is statistically distributed, which will result in a strong rotational cooling. The translational energy release in the OH will be low. Either the OH rotational energy, E_{rot}, is completely transferred into H_2O internal energy or E_{rot} is transferred into orbital angular momentum. But due to the large mass of the oxygen this will result only in low translational energy.

As some of the experiments were also carried out with $H_2{}^{18}O$, both ^{16}OH and ^{18}OH molecules were produced. The collision partner in the isotopically labelled experiment was always pure $H_2{}^{18}O$. From the results of the preceding paragraph we definitely see that the amount of ^{16}OH and ^{18}OH in the relaxed distribution is always in a direct proportion to the amount in the nascent distribution, which strongly suggests that in the collision complex an atom exchange does not take place. In the latter case the most likely result would be isotopic scrambling. We therefore conclude that, irrespective of the nature of the intermolecular potential, the "bond" which is formed in the collision will also break after the collision. The experiment involving $H_2{}^{18}O$ indicates that the chemical identity is preserved in the inelastic collision.

Many cases are known in which very large cross sections are observed for rotational relaxation of dipolar molecular pairs colliding under the condition of the sudden limit [19], but the observed high probability for rotational relaxation of OH by H_2O molecules is not expected from the classical treatment of rotationally inelastic collisions. The rotational energy of the colliding OH molecules is high (rotational states up to high quantum numbers are excited), so that their rotational period is short. Although the average kinetic energy of nascent OH greatly exceeds thermal energy ($v_{thermal} < v < 6v_{thermal}$), the collision time, τ_{col}, for most of the molecules is larger than the rotational period τ_{rot}.

As the potential between the two polar molecules is proportional to r^{-3}, the fast rotation of the molecules causes a "preaveraging" over all orientations which eliminates the odd-parity r^{-3} term, so that in this limit the predicted dipole–dipole cross sections are not very much larger than ordinary van der Waals cross sections [18].

Generally speaking the high rotational period of the majority of the OH radicals causes the system to be in the adiabatic limit. As a consequence, we should expect the rotational relaxation to be moderately slow. The results shown in fig. 1, and also table 1, demonstrate that the collisional pair OH–Ar behaves in the manner discussed above. We do not observe an effect from inelastic collisions in this case, when 40 Torr of argon are added. Assuming a 10% uncertainty in the experimenta data, the maximum cross section is less than 3 Å^2 for the collisional pair OH–Ar. The energy transfer is not efficient because the perturbation by collisions is slow. The rotator can accommodate itself to the perturbation. The observation that rotation-to-translation energy transfer in H_2 at room temperature requires an average of several hundred collisions, in contrast with 1–10 collisions for other homonuclear diatomics, supports this conclusion [22].

The simple mode presented permits one to argue that the formation of a hydrogen bond is a possible explanation of the experimental results. A more exact description could only follow from a detailed theoretical treatment of the problem. A very similar model has been discussed in connection with the observation of extremely efficient vibrational relaxation of HF(v=1) in collisions with H_2O and D_2O [20] and of moderately efficient vibrational relaxation of OH(v = 1) in collisions with H_2O [21].

Another approach would be to discuss the problem of rotational relaxation in terms of an energy gap law, the OH being caused to move up and or down the rotational ladder. Exponential [22] and inverse power laws [23] have been presented in the literature. Application of the widely used exponential gap law leads to the following expression for the rate constant for the quantum state transition $i \rightarrow f$:

$$k^{e}_{i\rightarrow f} \propto \exp(-\Theta|E_i - E_f|) ,$$

in which Θ is to be empirically fitted to the data and $E_i - E_f = \Delta E$ is the energy difference between the ith and the fth energy level. The statistical power gap law describes the dependence of the rate constant $k^{p}_{i\rightarrow f}$ on the energy transferred as follows:

$$k^{p}_{i\rightarrow f} \propto |E_i - E_f|^{-\alpha} ,$$

α being also empirically fitted. The two expressions lead to the same result in the limiting case $\Theta \to 0$ and $\alpha \to 0$.

Levine et al. [24] have investigated the rotational relaxation within a given vibrational manifold and shown that, for $\Theta \to 0$, an analytical solution is possible, and the entire distribution can be viewed as a superposition of two temperature distributions. These are the nascent distribution, whose relative weight diminishes with time, and the equilibrium distribution, whose relative weight increases with time. Interestingly, the OH energy distribution in the presence of water shows just such a superposition of two distributions.

The rotational relaxation of OH in collisions with water vapor is of considerable interest for atmospheric measurements, e.g., the detection of atmospheric OH in ambient air with the aid of laser induced fluorescence (LIF). These measurements suffer from a severe interference effect which originates from the photoinduced production of OH by the monitoring laser beam itself. Thus a composite signal is observed, partly from the artificially produced OH. In two recent papers [9,11] this effect was discussed in detail but without considering rotational relaxation. The results of the present paper show that the interference effect is further enhanced by the fast rotational relaxation of OH, since it additionally populates OH rotational states in low quantum numbers within the nanosecond detection time.

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