NANOSECOND SPECTROSCOPY: KINETICS OF STATE SELECTED SPECIES

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ABSTRACT

OH is chemically produced by photolysis of ozone in a $O_3/H_2O$ mixture with a nanosecond uv laser pulse. The OH-radicals were observed immediately after their formation nearly collision free by measuring the absorption intensities of the $X^2\Pi_{3/2}$ ($v'' = 0$, K") $\rightarrow$ $A^2\Sigma^+$ ($v' = 0$, K") transitions. The scanning of the rotational spectrum is performed by pressure tuning of the dye laser.

The population of the $\Lambda$ - doublets can be described by two different rotational temperatures. In the four lowest rotational states we observe inversion and in the higher rotational states antiinversion in the $\Lambda$ - doublets. For K" $\geqslant$ 7 there is a strong deviation from these thermal distributions.

There is a great interest to determine the distribution of rotational, vibrational and translational energy among the products of exothermic reactions. As the OH molecule plays an important role in atmospheric chemistry an attempt was made to study the formation of OH from the reaction of metastable oxygen atoms with water molecules which is the major formation mechanism in the atmosphere. The uv photolysis of ozone is the source of metastable $O(^1D)$ atoms, which react with $H_2O$ to produce OH according to the reaction

$$O(^1D) + H_2O \rightarrow OH + OH + 29 \text{ Kcal} \qquad (1)$$
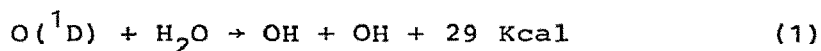
The fourth harmonic of a Nd-Yag laser at 266 nm forms the photolysis beam. All experiments to be described in the following were carried out with ozone at 2 torr and $H_2O$ at 10 torr.

Part of the second harmonic of the laser pumps a dye laser which is pressure tuned and frequency doubled to monitor the OH molecules. As the excited oxygen atoms in the system need a certain time to react with water the second harmonic of the Yag laser is optically delayed (20 ns). From the known rate constant of reaction (1) and the concentrations of the gases we calculate a reaction time of about 13 ns to form the OH (ref. 1). Observations at 60 ns delay time show that rotational relaxation will not influence the data taken at 20 ns.

In order to eleminate the influence of fluctuations of the dye laser the monitor beam is split into two beams one of which is traversing the cell the other one is passing by. The signals of the detectors are processed in a differential amplifier and a boxcar integrator. This technique is sensitive up to an absorption of 0.1 %, so that very accurate absorption measurements can be carried out.

In the OH radical the electronic ground state is a $^2\Pi$ state. The electron spin has the value 1/2 which produces two different states, $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$. Each rotational state is $\Lambda$ - doubled. Observations of the transitions of the electronic ground state $X^2\Pi_{3/2}$ (v"= 0,K") to the first excited electronic state $A^2\Sigma^+$(v' = 0,K') were made (ref. 2). The absorption intensities are proportional to the population of the state and the corresponding transition propability. Therefore we can calculate the number densities of OH in the different $\Lambda$ - doublet rotational states using the known oscillator strengths (ref. 2,3).

Our measurements of the population distribution are shown in Fig. 1. The experimental data represent the population of the individual rotational sublevels divided by their degeneracy. $\Pi_+$ represent the upper and $\Pi_-$ the lower $\Lambda$ - component.

If we assume that the experimental results are described by a straight line in this representation we can define a temperature for each of the two different distributions and each distribution refers to one of the two levels of a specific $\Lambda$ - doublet.
The results in fig. 1 indicate that the $\Lambda$ - doublets of the $^2\Pi_{3/2}$ manifold show population inversion for K = 1 up to 4 and antiinversion for higher rotational states. It should be mentioned that there are some deviations of the experimental data from a straight line behaviour which cannot be described by experimental errors.
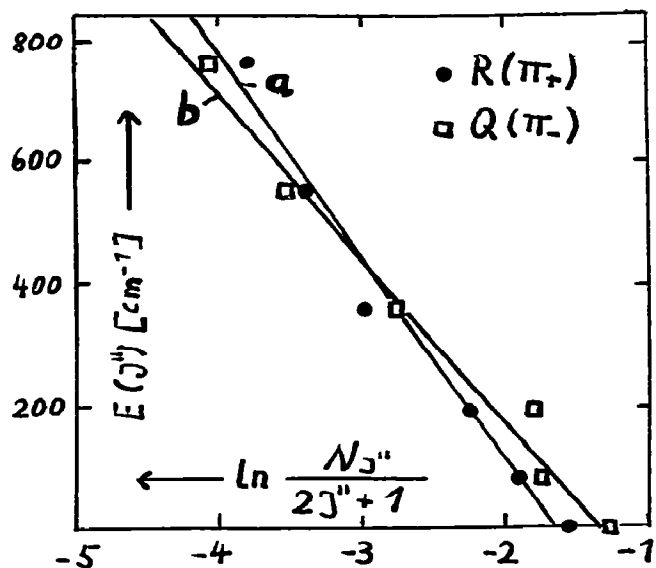
Fig. 1. Plot of $Ln(N_J"/2_J"+1)$ versus rotational energy $E(J")$ of different $\Lambda$ - doublets in the $^2\Pi_{3/2}$ ($v" = o$) state.

For higher rotational states $(K \geq 7)$ we get strong deviations from this calculated distribution. In fig. 2 the abscissa axis represents the quantum number $K"$ and the rotational energy in wavenumbers, respectively. The ordinate axis represents the logarithm of the ratio of the measured population to those numbers given by the thermal distribution represented by curve a, fig. 1. This means that we get a horizontal straight line and any deviation from this line indicates a deviation from the calculated thermal distribution.

For K greater six there is a very strong deviation; but also this experimental data are situated on a straight line, therefore it is possible to describe this behaviour by a thermal distribution. This distribution corresponds to a rotational temperature of 1700 K.

In our absorption measurements we determine the sum of the population of the two OH radicals formed in the reaction (1). One OH molecule originates from the old OH bond in water while the other one is new formed. The measured distributions which are very different can correspond to the old and the new bond, respectively. As the reaction is exothermic the reaction energy of 29 Kcal per mol has to be distributed on the products.

All measurements were carried out in the vibrational ground state, the energy distribution of the rotational states has been determined, consequently the translational energy would have to supply the remaining energy.
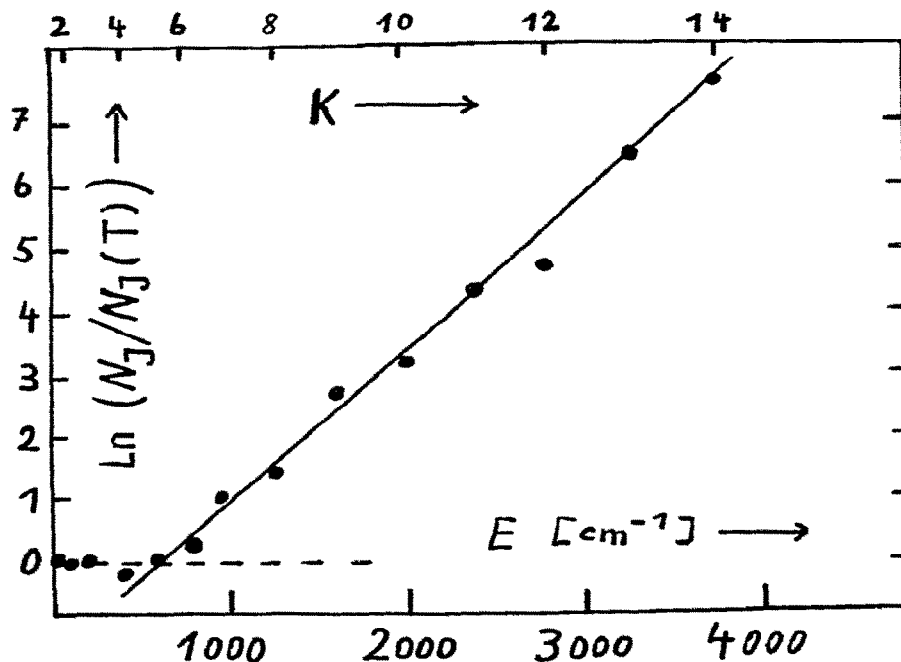
Fig. 2. Plot of Ln $(N_J/N_J(T))$ versus the rotational energy in the $^2\Pi_{3/2}(v" = o)$ state.

The translational energy can be deduced from the measured absorption linewidth which is proportional to the average translational velocity of the OH radicals. Recent measurements have shown, that the translation contains most of the exothermic energy of the OH-radicals formed in the lowest vibrational state.

REFERENCES

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