

INVERTED AND ANTI-INVERTED POPULATIONS OF Λ DOUBLETS OF CHEMICALLY PRODUCED OH

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With the aid of nanosecond laser flash photolysis OH is chemically produced and observed "collision free". The rotational states show inverted population in the Λ doublets $J' = 3/2, 5/2, 7/2$, and $9/2$ of ${}^2\Pi_{3/2}$ and anti-inversion in the higher rotational states. The intensities of the main and satellite absorption lines further indicate an inversion in special hyperfine states. Application to interstellar OH maser emission is considered.

Since microwave emission from interstellar OH has been observed, much work has been devoted to calculate conditions for inversion and anti-inversion of OH molecular states. The 18 cm line of OH is the first molecular line discovered by radio techniques [1]. Subsequent observations of the 18 cm OH emission led to the suggestion that maser amplification is involved [2]. These OH maser sources have been divided into several categories: type I, type IIa, and IIb, differing in their emission properties. Whereas type II sources are thought to originate from infrared pumping mechanisms, type I may be the result of chemical processes, although these latter sources have been the subject of a large number of pumping theories [3]. The theoretical treatment was able to give an explanation of special features, but there is still lack of a comprehensive description of the phenomena.

While OH is of great interest in "interstellar chemistry", this same molecule plays also an important role in atmospheric chemistry. For that reason an attempt was made to study the formation of OH from the reaction of metastable oxygen atoms with water molecules, which is a major formation mechanism in the atmosphere. Therefore we have set up an experiment to produce and observe OH radicals under special conditions. The UV photolysis of ozone is the source of metastable $O(^1D)$ atoms which react chemically with H_2O to produce OH according to the reaction



The experimental apparatus is depicted in fig. 1. The fourth harmonic of a Nd-Yag laser at 266 nm forms the photolysis beam. 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. All experiments to be described in the following were carried out with ozone at 2 Torr and H_2O at 10 Torr and $T = 298$ K. Pressures are controlled by a capacity manometer. The gases are continuously flowing through the cell which has a length of 2 cm.

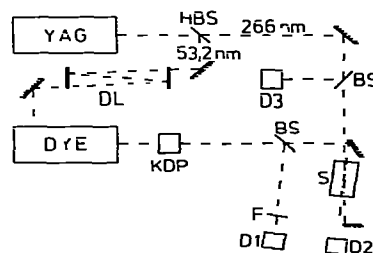


Fig. 1. Schematic drawing of the experimental arrangement. HBS: harmonic beam splitter, DL: delay line, BS: beam splitter, S: sample, F: filter; D: detector.

The photolysis beam is reflected to pass the system twice in order to form an $O(^1D)$ concentration within the beam path as homogeneous as possible. The diameter of the monitoring dye-laser beam is always smaller than that of the photolysing beam.

The time profile of the two beams is characterised by 7 ns and 6 ns halfwidths, respectively. The delay time between the two light pulses was kept constant at 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 [4]. The OH radicals produced in the reaction therefore suffer at most one collision in the system. We consider this to be an approximately collision-free experiment as far as OH is concerned. The influence of collisions was studied by observing the reaction also at 60 ns delay time. These measurements show that rotational relaxation is faster than expected but does not influence the results taken at 20 ns.

It should be mentioned that observation of the OH radicals is carried out by their UV absorption. Therefore the monitor beam is split into two beams, one of which is traversing the cell, the other one passes by. The signals of the detectors are processed in a differential amplifier and a boxcar integrator. This technique is sensitive up to $I_{\text{abs}}/I_0 < 0.1\%$, so that very accurate absorption measurements can be carried out.

Fig. 2 represents that part of the OH level diagram which is of importance for the discussion of the results. Observation of the $X^2\Pi_{3/2,1/2}(v''=0, J'') \rightarrow A^2\Sigma^+(v'=0, J')$ transitions was made. Five branches were registered for the spin component $^2\Pi_{3/2}(R_1, P_1, Q_1, Q_{21}, R_{21})$ and three for the spin component $^2\Pi_{1/2}(R_2, Q_2, Q_{21})^\ddagger$. As the hyperfine splitting in the rotational ground state is of the order of 50 MHz this splitting cannot be resolved. From the intensities of the rotational transitions in the different lines we can calculate the number densities of OH in the different rotational states using the known oscillator strengths [6].

Results are in fig. 3. This figure contains the information from measurement of the Q_1, R_1, Q_{21} , and R_{21} lines for $K'' = 1-6$. As the main and satellite lines originate from the same initial rotational state,

[‡] The rotational branch terminology is that normally employed for OH; see ref. [5].

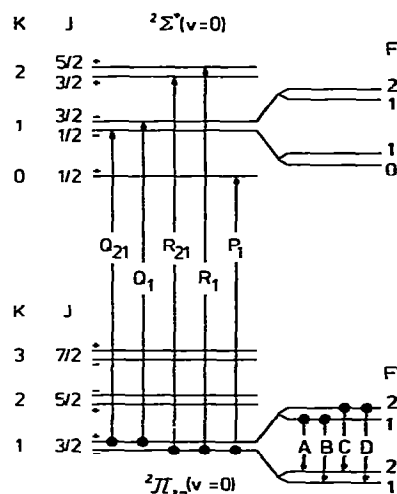


Fig. 2. Rotational level diagram of $X^2\Pi_{3/2}(v''=0, J'') \rightarrow A^2\Sigma^+(v'=0, J')$ transition, showing schematically fine-structure and hyperfine-structure splitting and $Q_1(1), Q_{21}(1), R_1(1), R_{21}(1),$ and $P_1(1)$ transitions. A, B, C and D describe the microwave transitions of the 18 cm OH line. (A: 1612 MHz, B: 1665 MHz, C: 1667 MHz, D: 1720 MHz). The rotational branch terminology is that normally employed for OH [5]. The diagram is not to scale.

e.g. $Q_1(1)$ and $Q_{21}(1)$ (see fig. 2), the number densities calculated from the line intensities should be the same for each such pair. Hence, the arithmetic mean of the respective Q and R pairs is taken. These values are in fig. 3 and are characterised by $Q(\Pi^+)$ or $R(\Pi^-)$, respectively. As the absorption intensity $I_{\text{abs}} = I_0 - I_T$

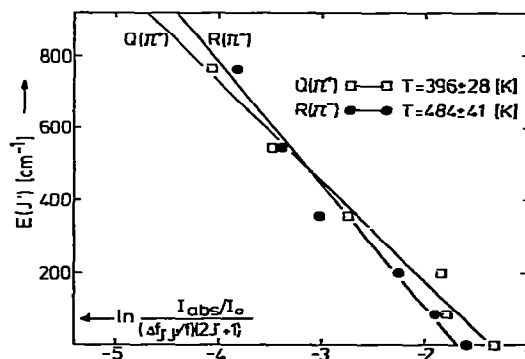


Fig. 3. Plot of $\ln \left\{ \frac{I_{\text{abs}}}{I_0} \left[\frac{\Delta f_{J''} J''}{f} (2J'' + 1) \right]^{-1} \right\}$ versus rotational energy $E(J'')$ of different A doublets of OH $^2\Pi_{3/2}(v''=0)$.

is proportional to the relative population of OH in each state and the corresponding oscillator strength, we get

$$I_{\text{abs}} \propto (\Delta N_{J''}/N) \Delta f_{J''J'}/f. \quad (2)$$

For a temperature T

$$\Delta N_{J''}/N = [(2J'' + 1)/Q_r] \exp[-E(J'')hc/kT], \quad (3)$$

$E(J'')$ and Q_r representing the energy of the rotational state J'' and the rotational partition function. From (3),

$$\ln \left[\frac{I_{\text{abs}}/I_0}{(\Delta f_{J''J'}/f)(2J'' + 1)} \right] = G - \frac{E(J'')hc}{kT}. \quad (4)$$

This function is in fig. 3 for the Q and R lines. The experimental results represent the population of the individual rotational sublevels divided by their degeneracy.

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 distributions. Each distribution refers to one of the two levels of a specific Λ doublet. Then it follows that the population of the OH molecules in the different Λ doublet components is described by an individual apparent rotational temperature as indicated in the insert in fig. 3. The results in fig. 3 indicate that the Λ doublets of the ${}^2\Pi_{3/2}$ manifold show population inversion for $J'' = 3/2, 5/2, 7/2$, and $9/2$ and anti-inversion for J'' higher than $9/2$.

It can be deduced from fig. 3 and eq. (4) that we can directly determine the difference Δn in the population of two relevant Λ doublet states from the difference between equivalent positions in the temperature representations. These values are given in table 1, column 2 showing the values determined from the experiment, and column 3 showing the values calculated from the temperature representations. It should be mentioned that there are some deviations of the experimental results from a straight line which cannot be described by experimental error. Especially the results for $Q_1(2)$ and $Q_1(3)$ always show the same behavior, that $Q_1(2)$ is to the left and $Q_1(3)$ to the right from the calculated temperature distribution.

In addition to the observation of population inversion and anti-inversion as a result of reaction (1), there is another phenomenon which follows from the measurements.

Table 1

Values of Δn ^{a)} from the individual experimental results (exp) and from the temperature distributions (temp), taken from fig. 3. $N(\Pi^+)$ is always the number density $\Delta N_{J''}$ of the upper component of the Λ doublet, and $N(\Pi^-)$ vice versa

J''	Δn_{exp}	Δn_{temp}
3/2	0.15	0.17
5/2	0.04	0.14
7/2	0.20	0.10
9/2	0.13	0.05
11/2	-0.03	-0.01
13/2	-0.12	-0.09

$$^a) \Delta n = [N(\Pi^+) - N(\Pi^-)] / [N(\Pi^+) + N(\Pi^-)].$$

It can be seen from fig. 2 that e.g. both $Q_1(K)$ and $Q_{21}(K)$ transitions refer to the same initial state but differ in their respective final states $J' = J''$ or $J' = J'' + 1$. When using the correct transition probabilities one should expect to deduce from these two transitions identical for the populations for the initial state. But this was never the case, using the transition probabilities as given by Earls [6]. Instead these number densities were always found to deviate up to 25%, being different in different rotational states. We propose the following explanation for our experimental findings:

Each Λ doublet component is split into two levels characterised by the quantum number F due to the interaction of nuclear spin I with the total angular momentum J . This is demonstrated in the level diagram of fig. 2 for the lowest rotational state $J'' = 3/2$ of ${}^2\Pi_{3/2}$. The transitions $Q_1(1)$ and $Q_{21}(1)$ couple the ground state with rotational states in the ${}^2\Sigma^+$ manifold with quantum numbers $J' = 3/2$ and $1/2$, the corresponding F values being 1 and 2, and 0 and 1, respectively. Due to the selection rule $\Delta J = +1$, the upper states of the $R_1(1)$ and $R_{21}(1)$ transitions are described by the quantum numbers $J' = 5/2$ and $3/2$ and therefore have F quantum numbers 3 and 2, or 2 and 1, respectively. From the rigorous selection rules $\Delta F = 0, \pm 1$ and $F = 0 \nrightarrow F = 0$, it follows that there is a different number of transitions if $Q_1(K)$ or $Q_{21}(K)$ lines are considered. The same is true for $R_1(K)$ and $R_{21}(K)$ lines. In case of a non-thermal distribution of the different hyperfine states, this will influence the intensities of the main and

satellite transitions of each pair to a different extent. As we do not have at the moment definite information on the probability of specific hyperfine transitions we can only speculate from general rules and information from the infrared and microwave spectrum [3].

If we normalize the expressions

$$\left[\frac{I_{\text{abs}}}{\Delta f/f} \right]_{R_{21}} \left\{ \left[\frac{I_{\text{abs}}}{\Delta f/f} \right]_{R_1} \right\}^{-1}$$

and

$$\left[\frac{I_{\text{abs}}}{\Delta f/f} \right]_{Q_{21}} \left\{ \left[\frac{I_{\text{abs}}}{\Delta f/f} \right]_{Q_1} \right\}^{-1},$$

which are indicative for the level population, to one for the case of a thermal distribution, then any measured deviation of these ratios from one indicates a non-thermal population in the different hyperfine levels. If we assume the absorption intensities to be proportional to the degeneracies of the states, then a ratio larger than one is indicative of a population anti-inversion for the two hyperfine states of the same Λ component, whereas the reverse is true in the case that these ratios are smaller than one. From the measurements we obtain the following values for $J'' = 3/2$ of ${}^2\Pi_{3/2}$,

$$\left[\frac{I_{\text{abs}}}{\Delta f/f} \right]_{R_{21}(1)} \left\{ \left[\frac{I_{\text{abs}}}{\Delta f/f} \right]_{R_1(1)} \right\}^{-1} = 0.88$$

and

$$\left[\frac{I_{\text{abs}}}{\Delta f/f} \right]_{Q_{21}(1)} \left\{ \left[\frac{I_{\text{abs}}}{\Delta f/f} \right]_{Q_1(1)} \right\}^{-1} = 1.10.$$

Referring to the level scheme shown in fig. 2, this means that the upper Λ doublet is anti-inverted in the two different hyperfine levels and the lower Λ doublet is inverted.

As a consequence the spectroscopic conditions for maser emission are most favorable in the case of the $F = 1 \rightarrow F = 1$ main transition (B line, see fig. 2) with frequency 1665 MHz. This is also the strongest emission line of a type I interstellar OH maser [3]. Due to the much lower transition probability of the $F = 1 \rightarrow F = 2$ transition (A line at 1612 MHz) we expect this emission to be weaker. The $F = 2 \rightarrow$

$F = 1$ transition (D line at 1720 MHz) and the $F = 2 \rightarrow F = 2$ main transition (C line at 1667 MHz) are possible with low amplification. We can summarize from the observations demonstrated in fig. 3 that due to population inversion in the doublets of $J'' = 5/2, 7/2$ and $9/2$ the necessary condition for maser emission is also given. Except for $J'' = 9/2$ these interstellar masers are observed [2,3].

The observations further show that related to a temperature distribution as indicated in fig. 3, nearly half of the OH molecules from reaction (1) are formed in the vibrationless state. As the reaction is exothermic, we expect to find the other half in higher excited states as was observed [7]. Our own absorption measurements indicate for the higher rotational states ($K > 7$) strong deviation from these thermal distributions.

It is interesting to note that in the reaction



Mariella and Luntz [8] observed population anti-inversion for rotational levels $K'' > 7$. In the same reaction ter Meulen et al. [9] found population inversion in the Λ doublets for $K = 1, 2$ and 3, but in this case the experiment was not collision free so that the authors could not exclude a collision mechanism via the decay of excited states. These results strongly indicate a similar behavior as in our experiment. It seems possible that the observations discussed in this paper are part of a more general phenomenon.

A few remarks should be made concerning the chemical pumping of interstellar OH masers. We cannot exclude that other OH-forming exothermic reactions also show population inversion. A possible candidate could be the fast reaction \ddagger



which is much more probable in interstellar media than reaction (1) because of the higher abundance of H_2 . But in addition to inversion, processes must be found which depopulate the OH ground state to maintain population inversion. Although the reaction



is exothermic, its activation energy makes this reaction effective only in the warmer regions of the clouds. The oxygen atom reacts quickly, destroying one more

\ddagger For special rate constants of reactions (6)–(9) see ref. [10].

OH and forming a hydrogen atom again, thus starting a chain,



CO, which is present to a much smaller extent than H, reacts very quickly with OH to start the same chain mechanism,



Both reactions (8) and (9) are fast under all thermal conditions. Photodissociation of OH provides a further sink for the OH molecules.

Besides the investigation of higher rotational and vibrational states of OH formed in reaction (1), we shall prove the possibility of forming an inverted population of OH in reaction (6)

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References

- [1] S Weinreb, A H Barrett, M L Meeks and J C Henry, *Nature* 200 (1963) 829
- [2] S. Weinreb, M L Meeks, J C. Carter, A.H Barrett and A E E Rogers, *Nature* 208 (1965) 440, R X McGee, B J Robinson, F.F. Gordner and J.G. Bolton, *Nature* 208 (1965) 1193, A H Barrett and A E E Rogers, *Nature* 210 (1966) 188.
- [3] M M Litvak, *Astrophys J.* 156 (1969) 471; M Ehtzur, P. Goldreich and N. Scoville, *Astrophys. J.* 205 (1976) 384; M M Litvak, A L McWhorter, M L Meeks and H J. Zeiger, *Phys. Rev Letters* 17 (1966) 821; J D Johnston, *Astrophys J* 150 (1968) 33, P M. Solomon, *Nature* 217 (1968) 334; W.D. Gwinn, B E. Turner, W M Goss and G L. Blackman, *Astrophys J.* 179 (1973) 789.
- [4] J A Davidson, C.M Sadowski, H J Schiff, G.E. Streit, C J Howard, D A Jennings and A L. Schmeltekopf, *J Chem. Phys* 67 (1977) 5021.
- [5] G H Dieke and H M Crosswhite, *J. Quantum Spectry. Radiat Transfer* 2 (1962) 97.
- [6] L Earls, *Phys. Rev* 48 (1935) 428.
- [7] R. Engleman, *J. Am. Chem Soc.* 87 (1965) 4193.
- [8] R P. Mariella Jr. and A C Luntz, *J. Chem Phys* 67 (1977) 5388.
- [9] J.J ter Meulen, W L. Meerts, G W M van Mierlo and A Dymanus, *Phys. Rev. Letters* 36 (1976) 1031.
- [10] R F Hampson Jr and D. Garvin, National Bureau of Standards Note 866 (1975).