Journal of Molecular Structure, 61 (1980) 239—242

INTENSITIES OF THE ROTATIONAL SPECTRUM OF OH ($^2\Sigma^+(v' = 0, J') \leftarrow {}^2\Pi_{3/2}\ (v'' = 0, J''))$)

G. Ortgies, K.-H. Gericke, F. J. Comes
Institut für Physikalische und Theoretische Chemie an der
Universität Frankfurt a.M. (F.R.G.)

ABSTRACT

The observation of the OH radicals, formed in the reaction of $O(^1D)$ atoms with water, was carried out by their uv absorption. The four branches Q_1, Q_{21}, R_1 and R_{21} were registrated for the rotational states $K'' = 1$ to $K'' = 6$. The measured intensity ratios of corresponding main and satellite lines deviate strongly from those calculated from the transition probabilities. A non thermal population of the hyperfine levels, resulting from the reaction is supposed and the consequence for maser amplification will be discussed.

The 18 cm line of OH, originating at interstellar sources, is the first molecular line discovered by radio techniques. The extraordinary nature of this radiation led to the suggestion that maser amplification is involved (ref. 1). Neccessary condition for maser amplification is a population inversion of two states. One possible pumping mechanism for a population inversion can be the result of a chemical process. OH radicals, formed in the reaction of $O(^1D)$ - atoms with water show a population inversion in the Λ - components of $J'' = 3/2$, $5/2$, $7/2$, and $9/2$ (ref. 2). The results of our absorption measurements will be discussed in this paper with respect to possible maser amplification.

For a better understanding of the discussion of the results, part of the OH level diagram is represented in fig. 1. In the electronic ground state the OH radical exhibits the two spin components $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$. In the figure the rotational states of the $^2\Pi_{3/2}$ state are shown. Each of these states is split by Λ - doubling, an interaction between the rotation of the nuclei and the motion of the unpaired electron in its orbit. Hyperfine interaction with the unpaired spin of the proton further splits the levels.

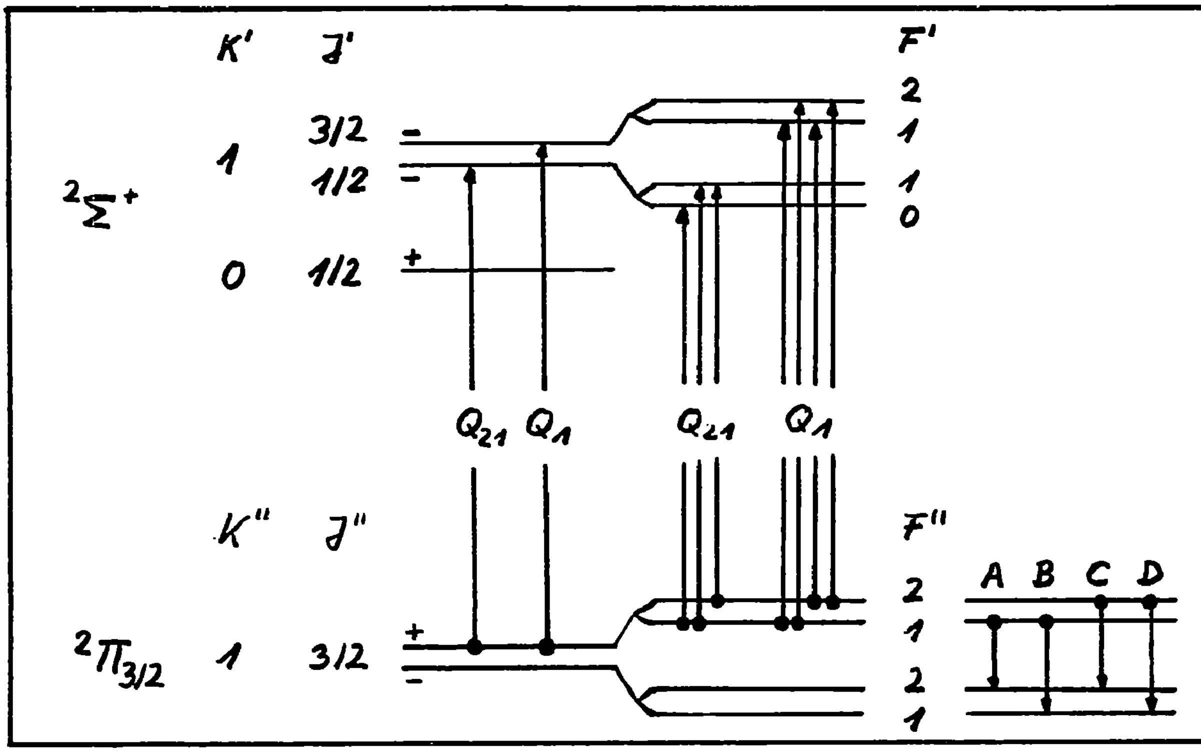

Fig. 1. Part of the OH rotational level diagram of the ground state and the first excited electronic state, including the main and satellite Q-transitions and the hyperfine maser lines for K"=1 (A: 1612 MHz, B: 1665 MHz, C: 1667 MHz, D: 1720 MHz).

Due to the selection rules for J and K, six rotational branches are possible for each spin component. In our measurements the four branches Q_1, Q_{21}, R_1, and R_{21} were analysed for the rotational states K"=1 to K"=6. In the figure the corresponding main and satellite lines Q_1 (1) and Q_{21} (1) are represented on the left. It can be seen, that these two lines originate from the same Λ - level and differ only in the spin component of the upper state. The same is true for the two R-branches.

As the absorption intensity is proportional to the transition probabilities and the population of the initial state, this population can be determined for each transition, using the known transition probabilities (ref. 3). Because corresponding main and satellite lines refer to the same initial state, one should expect to calculate identical populations from the absorption intensities of both lines. But this could be found in no case. Instead these populations were always found to deviate up to 25 %.

Our first intension to explain these results was the assumption, that we used wrong transition probabilities. The only free parameter in the formulas of the transition probabilities is the so-called coupling constant a, describing the intermediate case for the spin orbit coupling between Hund's case a) and b). The determination of the coupling constant from our measurements gave different values for the observed rotational states in contradiction to the theory. This could not be explained with experimental errors. In addition, our values of the coupling constant deviate strongly from those, obtained by other authors (ref. 4). Therefore we cannot believe, that wrong transition probabilities are the reason for the unexpected intensity ratios of corresponding main and satellite lines.

As represented in the figure, each Λ - doublet is split into two levels characterized by the quantum number F. From the rigorous selection rule $\Delta F = 0, \pm 1$, and $F = 0 \not\rightarrow F = 0$ it follows, that there is a different number of transitions if the main or satellite line is considered. For the main branch Q_1 four transitions are possible for each rotational state, whereas for the corresponding satellite branch Q_{21} only 3 transitions can exist. Regarding the two R-branches, this results in three and four transitions for the main and satellite branch, respectively. In case of a non thermal population distribution in the hyperfine doublets this will influence the intensity ratios of the main and satellite lines. The line intensity is determined by the population of the single hyperfine states and their uv transition probabilities. As we do not have a definite information on the transition probabilities, we cannot determine these populations. For a thermal population distribution the ratio of the absorption intensity of corresponding satellite and main lines divided by the corresponding oscillator strengths must be one. Any measured deviation from one will indicate a non thermal population distribution in the different hyperfine levels. If we assume the absorption intensities to be proportional to the degeneracies of the hyperfine states, then a ratio larger than one is an indication of a population antiinversion for the two hyperfine states of the same Λ - component whereas the reverse is true in case that these ratios are smaller than one. From our measurements we get for J"= 3/2 of $^2\Pi_{3/2}$ a ratio of 0.88 for the R-branch and a ratio of 1,10 for the Q-branch. Refering to the level scheme, this means that the upper lambda doublet is antiinverted in the two different hyperfine levels and the lower one is inverted.

As a consequence the spectroscopic conditions for maser emission are most favorable in the case of F=1 → F=1 main transition with frequency 1665 MHz, as shown in the figure. Due to the much lower transition probability we would expect the F=1 → F=2 transition at 1612 MHz to be clearly weaker. Under our assumption also the transitions at 1667 and 1720 MHz are possible but only with low amplification. All these lines were observed in interstellar OH - masers.

We can further summarize from our measurements that due to population inversion in the lambda doublets of J"= 5/2, 7/2, and 9/2 the necessary condition for maser emission is also given. Until now these interstellar masers are observed except for J" = 9/2.

REFERENCES

1 S. Weinreb, M. L. Meeks, J.C. Carter, A. H. Barrett, and A.E.E.Rogers: Nature 208, 440 (1965).
R. X. McGee, B. J. Robinson, F. F. Gordner, and J. G. Bolton: Nature 208, 1193 (1965).
A. H. Barrett and A.E.E. Rogers: Nature 210, 188 (1966).
2 K.-H. Gericke, G. Ortgies, and F. J. Comes: to be published
3 L. T. Earls, Phys. Rev. 48, 423 (1935).
4 G. H. Dieke and H. M. Crosswhite, J. Quant.Spectrosc.Radiat.Transfer 2, 97 (1962).
M. Mizushima, Phys. Rev. A 5 (1), 143 (1972).
E. A. Moore and W. G. Richards, Physica Scripta 3, 223 (1971).