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Observations of Population Inversion between the Λ-Doublet States of OH

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Inverted population distribution between Λ-doublet states of OH produced in the reaction $H+NO_2 \rightarrow OH+NO$ has been observed in a beam maser and in a molecular-beam electric-resonance spectrometer. The observed inversions are of the order of 4–6% for the $^2\Pi_{3/2}$, $J=\frac{3}{2}, \frac{5}{2}, \frac{7}{2}$, and the $^2\Pi_{1/2}$, $J=\frac{1}{2}$ states, and less than 1% for the $^2\Pi_{1/2}$, $J=\frac{3}{2}, \frac{5}{2}, \frac{7}{2}$, and $\frac{9}{2}$ states.

Nonequilibrium population distributions of hydroxyl radicals have been reported for several types of production processes.[1-3] In all these cases the population distributions can be described by some positive excitation temperature. Population inversion between rotational states of the electronic ground state ($X^2\Pi$) of OH has been obtained by Ducas *et al.*[4] in their infrared OH laser. In the present investigation population inversion between the Λ-doublet levels has been observed for the OH radicals produced in the reaction[5]

$$H+NO_2 \rightarrow OH+NO. \quad (1)$$

Although this is the first report of "natural" inversion between closely spaced doublet levels, such inversions might be occurring in a wide range of reactive and collisional processes. The present results may be of direct importance for the understanding of reactive interactions involving diatomic $^2\Pi$ molecules. They might also contribute to the understanding of the elusive problem of the origin of the maser emission by the interstellar OH sources. Although a number of possible inversion mechanisms based on pumping by radiation[6] and by collisional[7] or reactive processes[8] have been proposed, no laboratory investigations in this field have been reported so far.

The measurements have been performed in a beam maser and in a molecular-beam electric-resonance (MBER) spectrometer. A description of the MBER spectrometer has been given elsewhere.[9] Details of the OH beam maser will be published in a forthcoming paper. The basic outline of the two spectrometers is schematically shown in Fig. 1. In both spectrometers the OH radicals were produced by the reaction (1) for which the atomic hydrogen was obtained from an electrodeless discharge at 2.45 GHz in H_2O. The reaction took place near the end of the flow tube where the NO_2 was injected via a capillary glass array or through a concentric ring of small holes. The reaction products were streaming freely into the source chamber. The molecular beam was formed by a hole with a diameter of 2–3 mm at a distance of a few millimeters from the end of the flow tube.

In the beam maser the Λ-doublet transitions were detected in two microwave cavities tuned to different transitions. The measurements have been performed on the Λ-doublet transitions in the rotational $J=\frac{3}{2}$, $\frac{5}{2}$, and $\frac{7}{2}$ states of the electronic $^2\Pi_{3/2}$ level. In normal operation, state se-

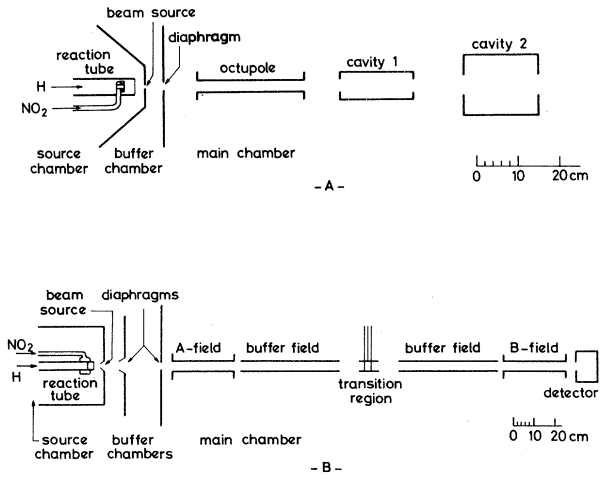

FIG. 1. Diagram of the molecular beam maser and the MBER spectrometer.

lection was performed using an electrostatic octupole resulting in a signal-to-noise ratio of about 100 at $RC = 1$ sec for the strongest main line transitions ($J = \frac{3}{2}$, $F = 2 \rightarrow 2$, and $J = \frac{5}{2}$, $F = 3 \rightarrow 3$) and of about 15 for the weakest lines ($J = \frac{7}{2}$). The satellite ($\Delta F = \pm 1$) transitions were much weaker and have not been investigated. The full linewidth of about 5 kHz was determined by the transit time of the molecules through the cavity.

In the MBER spectrometer the OH radicals in the upper Λ-doublet state of a given rotational state were focused on an ionization detector by two quadrupoles designated by A and B in Fig. 1(b). The Λ-doublet transitions were induced by a microwave field (C-field) applied between two parallel plates. The measurements have been done on the Λ-doublet transitions in the states $^2\Pi_{3/2}$, $J = \frac{3}{2}$, $\frac{5}{2}$, and $\frac{7}{2}$ and $^2\Pi_{1/2}$, $J = \frac{1}{2}$ up to $J = \frac{9}{2}$. The signal-to-noise ratio at $RC = 1$ sec varied between 100 ($^2\Pi_{3/2}$, $J = \frac{3}{2}$) and 10 ($^2\Pi_{1/2}$, $J = \frac{9}{2}$).

In both spectrometers the microwave transitions are of the $\Delta M_F = 0$ type and the intensity is proportional to

$$\sum_{M_F} |M_F| [N(+, F, M_F) - N(-, F', M_F)] \qquad (2)$$

where $N(+, F, M_F)$ and $N(-, F', M_F)$ is the population of the substate $|M_F\rangle$ of the upper $|+F\rangle$ and lower $|-F'\rangle$ Λ-doublet hyperfine state, respectively. In thermal equilibrium the relative population difference

$$\Delta N_{F,F'} = 2 \frac{N(+, F, M_F) - N(-, F', M_F)}{N(+, F, M_F) + N(-, F', M_F)} \qquad (3)$$

is equal to $-h\nu/kT$, varying between -2×10^{-4} at $\nu = 1.6$ GHz and -2×10^{-3} at 14 GHz (the highest transition frequency in the present investigation). By the application of state selection most of the molecules in the lower state are rejected out of the beam which results in the strong emission signals. In the absence of state selection, absorption signals are expected, far below the detection limit of both spectrometers. However, for all considered rotational states rather strong emission signals have been observed without any state selection. Apparently these signals originate in the population inversion ($\Delta N_{F,F'} > 0$) between the Λ-doublet states.

The results obtained with the beam maser are summarized in columns 1–4 of Table I together with the transition frequencies measured using the method reported earlier.[10] The values given in the third column represent the ratios of the intensities I_0 and I_s observed when all selector rods were grounded and when the selector was operating at 25 kV, respectively. The measurements have been performed using time-averaging techniques. Without state selection the signal-to-noise ratio was typically about 5 after 100 integrations at a sweep time of 16 sec. Both before and after each measurement the line was recorded a few times with state selection. The values given in Table I are the averaged results for 3 to 6 measurements performed on different days.

The inversion of the population between the upper $|+F\rangle$ and lower $|-F'\rangle$ hyperfine state can be calculated from the intensity ratios given in col-

TABLE I. The results of the OH beam-maser and MBER measurements. The microwave intensity with and without state selection is represented by I_s and I_0, respectively. The population inversion $\Delta N_{F,F'}$ between the two hyperfine states involved is defined in the text.

Transition Ω, J, $F \rightarrow F'$	Frequency (kHz)	Beam maser $100 I_0/I_s$	Beam maser $\Delta N_{F,F'}$	MBER $100 I_0/I_s$	MBER $\Delta N_{F,F'}$
3/2, 3/2, $1 \rightarrow 1$	1665 401.84(10)	0.93(9)	0.040(15)		
$2 \rightarrow 2$	1667 359.03(10)	0.34(8)	0.020(10)	2.4(5)	0.040(20)
3/2, 5/2, $2 \rightarrow 2$	6030 748.50(20)	1.38(13)	0.045(20)		
$3 \rightarrow 3$	6035 093.21(20)	0.82(7)	0.045(20)	2.2(5)	0.040(20)
3/2, 7/2, $3 \rightarrow 3$	13434 637.40(20)	1.02(25)	0.035(15)		
$4 \rightarrow 4$	13441 417.27(20)	0.93(19)	0.050(20)	2.5(6)	0.060(30)
1/2, 1/2, $1 \rightarrow 1$	4750 656(3)			2.4(5)	0.060(30)
1/2, 3/2, $2 \rightarrow 2$	7820 125(5)			0.5(3)	0.009(5)
1/2, 5/2, $3 \rightarrow 3$	8189 587(5)			0.3(2)	0.006(4)
1/2, 7/2, $4 \rightarrow 4$	5523 438(5)			0.4(3)	0.005(4)
1/2, 9/2, $5 \rightarrow 5$	117 149.5(10)			< 1.5	< 0.006

umn 3 of Table I using the relation

$$\Delta N_{F,F'} = \frac{I_0 \Omega_s}{I_s \Omega_0} \frac{\sum_{M_F} |M_F| [S(+, F, M_F) - S(-, F', M_F)]}{\sum_{M_F} |M_F|}, \quad (4)$$

where Ω_0 and Ω_s are the solid angle subtended at the beam source by the cavity and the state selector, respectively; $S(+, F, M_F)$ and $S(-, F', M_F)$ are the ratio of the number of the OH radicals in the upper $|F, M_F\rangle$ and the lower $|F', M_F\rangle$ substate, respectively, focused by the state selector into the microwave cavity, and the total number of OH radicals in the same substate which enter the selector within the solid angle Ω_s. It is assumed that the substates of the same hyperfine level are equally populated. The values for S have been obtained from computer calculations in which the molecular trajectories in the octupole were computed for each substate $|M_F\rangle$ at 50 values of the entrance angle and 60 values of the molecular velocity.[11] The resulting values for the population inversion are given in column 4 of Table I. The indicated errors represent mainly an estimated uncertainty of 20–30% in the trajectory calculations because of the fringe field effects.

In the MBER spectrometer the inversion signals were observed by switching off the polarizing quadrupole (A) and maintaining the analyzer field (B). When the initial populations of both Λ-doublet states of a given rotational state are equal no change in the detector signal is observed when transitions between the two states are induced by the microwave field. In the case of an inverted population distribution the net effect of the microwave field is emission, in the present geometry observed as a decrease of the detector signal. The measured intensity ratios and the resulting values for the population inversion calculated in the same way as the beam-maser results are summarized in the last two columns of Table I. In the case of the $^2\Pi_{3/2}$, $J = \frac{3}{2}$ and the $^2\Pi_{1/2}$, $J = \frac{1}{2}$ state both the $\Delta F = 0$ and the $\Delta F = \pm 1$ transitions were investigated, all showing emission signals corresponding to ΔN of 4–6%. Within the experimental accuracy there is no inversion between the hyperfine states of the same Λ-doublet state. The results for the $^2\Pi_{3/2}$ states are in good agreement with the values obtained in the beam-maser spectrometer.

In both experiments extensive test measurements have been performed to examine the possibility that the observed emission signals were caused by instrumental effects. The inversion signals showed the same line shape as the signals obtained with state selection and they disappeared when the injection of NO_2 or the microwave discharge was switched off. No signals were detected in the MBER spectrometer when both quadrupoles (A) and (B) were grounded or when other molecules (e.g., NO) were injected instead of OH. The most convincing evidence is the observation of the inversion signals in the beam-maser spectrometer when the state selector was removed. So the possibility that the emission signals were caused by electret formation or by charging of the insulators on which the selector rods are mounted is herewith ruled out.

Some preliminary investigations have been done to uncover the mechanism responsible for the population inversion. An obvious possibility is the production of OH radicals preferentially in the upper Λ-doublet states or in some excited rotational, vibrational, or electronic state, subsequent decay from which produces inversion of the Λ-doublets. However, it is also possible that inverting collision processes are taking place between the reaction zone and the beam source. Measurements at increased NO_2 flows or with H_2 molecules injected in the buffer chamber yielded smaller intensity ratios I_0/I_s from which it might be concluded that collisions with H_2 or NO_2 are destructive for the inversion. Replacement of H_2O by H_2 in the discharge producing atomic hydrogen did not result in any significant change in the inversion signals. This eliminates the possibility that the small fraction of OH produced in the dissociation of H_2O is inverted, or that collisions with O_2 are inverting. Also from the fact that no inversion effects have been reported in microwave-absorption experiments on OH produced by the reaction (1)[12,13] it may be deduced that molecular collisions are rather thermalizing than inverting. Collisions with electrons or other charged particles from the discharge are probably also not inverting as could be concluded from the lack of any changes in the inversion signals when a magnetic field was applied between the discharge region and the OH production zone. So strong indications are present that the reaction (1) is responsible for the anomalous Λ-doublet populations either directly or via the decay from an excited state. Effects of possible vibrational decay were investigated in the beam maser

by measuring the inversion signals as a function of the distance between the microwave cavity and the beam source. No indications of vibrational decay were obtained. Electronic decay proceeds very fast ($\sim 10^{-6}$ sec) and this inversion mechanism is still open. Further investigations on the origin of the population inversion are in progress.

It is seen from Table I that the laboratory inversion of Λ-doublet population is rather strong for the $^2\Pi_{3/2}$ states with $J = \frac{3}{2}$, $\frac{5}{2}$, and $\frac{7}{2}$ as well as for the $^2\Pi_{1/2}$, $J = \frac{1}{2}$ state. Strong emission lines from interstellar OH sources have been observed only for these states. In the case of the $^2\Pi_{1/2}$ states with $J \geq \frac{3}{2}$ much weaker inversions have been measured. Weak emission from the $^2\Pi_{1/2}$, $J = \frac{3}{2}$ state seems to have been reported recently,[14] after many fruitless searches. The reported[15] emission from the $^2\Pi_{1/2}$, $J = \frac{5}{2}$ state has been seriously questioned[16] and may be considered as unobserved. Emission from the $^2\Pi_{1/2}$, $J = \frac{7}{2}$ and $\frac{9}{2}$ states has not been observed. There is clearly a close correspondence between the population inversion in our OH production system and in the interstellar OH sources. Also the magnitude of the inversion is of the same order as the values considered in the several inversion models proposed for the interstellar OH masers. Although the possibility of an accidental correspondence cannot be excluded at the present stage of the experiments the results seem to support the hypothesis that the population inversion of interstellar hydroxyl radicals is generated during the reactive formation process.

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