

Selective Λ doublet population of OH in inelastic collisions with H₂: A possible pump mechanism for the $2\pi_1 / 2$ astronomical OH maser

P. Andresen, D. Häusler, and H. W. Lülf

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COMMUNICATIONS

Selective Λ -doublet population of OH in inelastic collisions with H_2 : A possible pump mechanism for the ${}^2\Pi_{1/2}$ astronomical OH maser

P. Andresen, D. Häusler, and H. W. Lülf

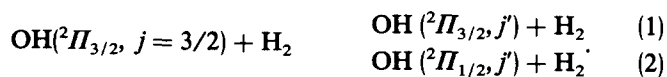
MPI für Strömungsforschung, Böttingerstraße 4-8, 3400 Göttingen, Federal Republic of Germany

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Inelastic and reactive collisions of OH play an important role in combustion, atmospheric chemistry and, as will be demonstrated here, in astrophysics. In this experiment we report the generation of a very intense, internally cold OH radical beam which is used in a cross beam experiment to study the inelastic collisions of OH with H_2 . These collisions have been proposed as a pump mechanism for the astronomical OH-Maser in the OH (${}^2\Pi_{3/2}, j = 3/2$) state.¹ It will be demonstrated, that this is wrong. However, the OH + H_2 collisions could explain the pump mechanism of the astronomical OH-maser in the OH (${}^2\Pi_{1/2}, j = 1/2$) state.²

The details of the experimental setup will be described later.³ The crucial part is the generation of the cold OH-radical beam by photolysis of $HONO_2$ at 193 nm (ArF excimer laser) in a small quartz capillary (1 mm ϕ , 10 mm length) which is mounted in front of a pulsed valve. In the subsequent expansion the hot OH radicals⁴ are cooled, yielding a beam of OH almost exclusively in the lowest quantum state OH (${}^2\Pi_{3/2}, j = 3/2$). Higher states are an order of magnitude less populated. The beam is so intense that a state to state scattering experiment with a secondary pulsed H_2 nozzle beam became feasible. The internal state distribution of OH is probed in the scattering zone by LIF via the ${}^2\Pi-{}^2\Sigma$ absorption band. The change in the fluorescence intensity for a given state of OH with the H_2 beam on or off, is a measure for the density of OH molecules formed in that particular state by collisions with H_2 . The densities can be interpreted as integral excitation cross sections because in the case of OH + H_2 collisions the flux density transformation⁵ is dominated by the CM motion.

In the inelastic collision of OH with H_2 we have to distinguish between the collisions within the ${}^2\Pi_{3/2}$ manifold (process 1) and the collisions leading to the ${}^2\Pi_{1/2}$ manifold (process 2)



In both cases we measure in addition to the rotational distributions the population in the Λ -doublet substates for a given j' .

Figure 1 shows the integral excitation cross sections for both process 1 (circles) and process 2 (squares) plotted versus the excitation energy of the final OH state. The arrow indicates the maximum available excitation energy, given by the CM collision energy of $\sim 680 \text{ cm}^{-1}$. The data are for R lines only, corresponding to the population in the $\Pi-\Lambda$ -doublet state.

The cross sections within the ${}^2\Pi_{3/2}$ manifold decrease rapidly with increasing excitation energy. The cross section for $j' = 7/2$ is more than a factor of 2 smaller than for $j' = 5/2$, indicating that the $\Delta j = 1$ coupling is stronger than the $\Delta j = 2$ coupling. This was also found by *ab initio* calculations^{1,6} and is explained by the polar character of the OH molecule.

For the ${}^2\Pi_{1/2}$ state the cross sections decrease slower with increasing excitation energy. The ratio of the cross sections for process 1 and process 2 is determined accurately in the experiment because the laser is just tuned to other frequencies. In comparison to the scattering of NO (${}^2\Pi_{1/2}, j = 1/2$) with rare gases,⁷ the fine structure changing collisions are ~ 6 times more probable. As shown by several authors,⁸ the scattering of ${}^2\Pi$ molecules is determined by two

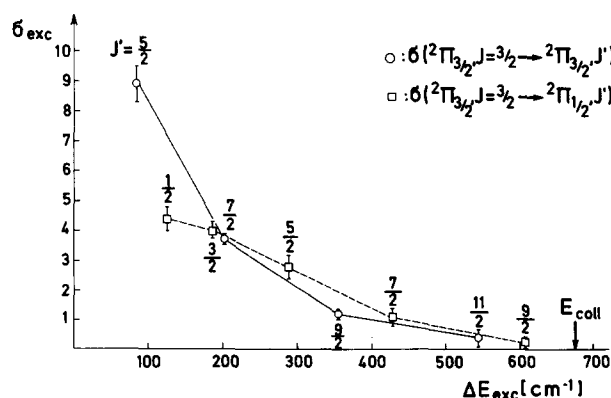


FIG. 1. Integral excitation cross sections for both ${}^2\Pi_{3/2}$ and ${}^2\Pi_{1/2}$ as a function of the excitation energy. The numbers at the symbols are for the final j' values.

potential surfaces, A' and A'' , which differ essentially in the orientation of the unpaired $p\Pi$ lobe relative to the collision partner. The fine structure changing collisions depend essentially upon the difference between A' and A'' . Thus the relatively large probability for fine structure transitions in $\text{OH} + \text{H}_2$ collisions indicates a large difference between A' and A'' .

Figure 2 shows the relative populations of the A -doublet substates for both process 1 (circles) and process 2 (squares) as a function of the final OH angular momentum j' . Plotted is the ratio of the fluorescence intensity of R lines relative to Q lines for a given j' . R lines measure the population in the Π^- - A -doublet state, whereas Q lines measure the population in the Π^+ - A -doublet.⁹ Here the $+/-$ refers to the electronic parity of the A -doublet states.

Figure 2 shows that with increasing j' an increasing preference of R lines is found for both processes. No preference is found for $j' = 5/2$ in the $^2\Pi_{3/2}$ and $j' = 1/2$ in the $^2\Pi_{1/2}$ manifold.

In the $^2\Pi_{3/2}$ manifold R lines measure the population in the energetically lower A -doublet state. The preference of R lines thus implies anti-inversion in the $^2\Pi_{3/2}$ manifold, eliminating $\text{OH} + \text{H}_2$ collisions as a pump mechanism for the astronomical OH ($^2\Pi_{3/2}$, $j = 3/2$) maser.

However, due to a reverse energetic ordering of the A -doublet states in the first five rotational states in the $^2\Pi_{1/2}$ manifold⁹ the preference of R lines in the $^2\Pi_{1/2}$ state implies inversion. Although no direct inversion is observed for $j' = 1/2$, inversion is created for larger j' . Due to optical selection rules, Π^- (Π^+) states always relax to Π^- (Π^+) states in the infrared relaxation. Summing up separately the cross sections for Π^- and Π^+ states, which will be the net result of the relaxation, we obtain 20% more in the energetically higher Π^- state for $^2\Pi_{1/2}$, $j = 1/2$. This could explain the astronomical OH maser in this state.

The physical reason for the selective population of A -doublet states has been given several times,¹⁰ and is briefly repeated here.

As seen by *ab initio* calculations,^{6,11} the potential surface favors a planar $\text{OH}-\text{H}_2$ geometry. The forces that are responsible for rotational excitation are located in the plane defined by the $\text{OH}-\text{H}_2$ collision complex, leading to OH molecules rotating preferentially in that plane. On the other hand, the unpaired $p\Pi$ -lobe of OH will be oriented towards the H_2 molecule, forming a partial chemical bond with one of the H atoms. Thus the $p\Pi$ lobe will also be oriented in the plane of the collision complex. This mechanism leads preferentially to OH molecules with the unpaired $p\Pi$ lobe in the OH rotation plane.

This is, however, the energetically lower A -doublet state in the $^2\Pi_{3/2}$ manifold, and not, as assumed in several theoretical attempts to explain the OH ($^2\Pi_{3/2}$) masers,^{1,12} the upper A -doublet state! It is only this wrong assignment of A -

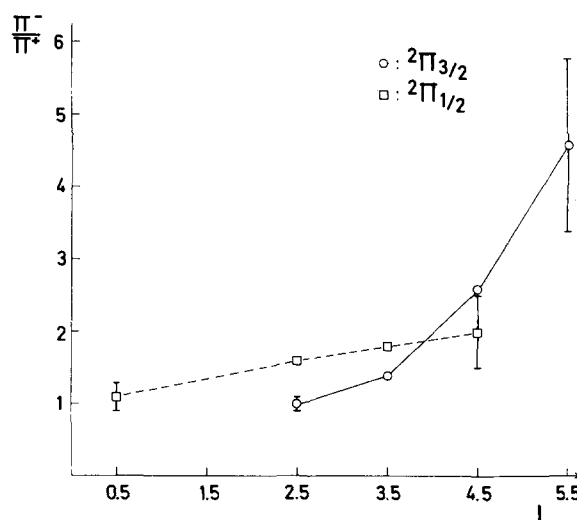


FIG. 2. Relative A -doublet population $\Pi^-/\Pi^+ = R/Q$ for both $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ as a function of final j' .

doublets that causes the discrepancy between our results and the theoretical predictions. This has been discussed recently in detail for the photodissociation of H_2O where the other A -doublet state of OH is preferentially populated.¹³ Photodissociation of H_2O is the most probable explanation of the pump mechanism for the OH ($^2\Pi_{3/2}$, $j = 3/2$) main line masers.

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