

Creation of Population Inversions in the Λ Doublets of OH by the Photodissociation of H_2O at 157 nm: A Possible Mechanism for the Astronomical Maser

P. Andresen, G. S. Ondrey, and B. Titze

Max Planck Institute für Strömungsforschung, D-3400 Göttingen, Germany

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Water molecules are photolyzed by a F_2 laser at 157 nm. The nascent OH (${}^2\Pi_{3/2}$, $v=0$) rotational state distribution, probed via laser-induced fluorescence, reveals a strong preference for populating the upper Λ -doublet component. The population inversion is found to be a function of both the initial temperature of the H_2O as well as the final rotational state in which the OH radical is formed. These results may provide a simple mechanism for the astronomical OH maser observed by others.

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The explanation for the astronomical OH maser has been a controversial issue since it was first observed in 1963.¹ Many theoretical arguments have been proposed² for creating the required population inversion in the ground state of OH(${}^2\Pi_{3/2}$). In general, the source of OH radicals in space is believed to be the photodissociation of water vapor.² However, present theories² invoke complicated collisional or radiation pumping schemes to form population inversions in the OH radicals. The experimental result of the present work shows that such involved mechanisms are unnecessary in that the population inversion is a direct result of the initial creation of the OH radicals by photodissociation from the 1B_1 state of water.

In the present experiment, two sources of water were used; either a flow system or a pulsed nozzle beam. The flow system is similar to that described previously,³ and provides a replenished source of room-temperature water vapor at $\sim 4 \times 10^{-5}$ Torr. The beam source is a modified fuel injection valve (Bosch). Conditions in the beam were such (20% H_2O in argon; $P_0 \sim 50$ Torr; nozzle diam, 1 mm) as to provide internally cold water molecules ($T_{\text{int}} \leq 50$ K)⁴ with minimum dimerization ($\propto P_0/d$).⁵

Water from the beam or cell is photolyzed with 157-nm radiation from a F_2 laser (Lambda Physik EMG 200). This is near the maximum of the first absorption band of water (1400–1900 Å) which has been ascribed⁶ to the $\tilde{A} {}^1B_1 - \tilde{X} {}^1A_1$ ($\pi^* - n$) transition. The 1B_1 state of water correlates with the formation of OH(${}^2\Pi$) + H(2S), the only photolysis products observed.⁶ Resulting OH(${}^2\Pi_{3/2}$) radicals are probed by laser-induced fluorescence⁷ via the $A {}^2\Sigma^+ - X {}^2\Pi_{3/2}$ transition,⁸ by using a Nd-doped yttrium aluminum garnet-pumped frequency-doubled dye laser. The probe laser is fired within 100 nsec of the dissociation laser to insure

against collisional relaxation of the nascent OH state distribution. Fluorescence is viewed through imaging optics by an RCA 31034 photomultiplier tube, and the signal collected in the manner described previously.³ Because the dye-laser power is high enough to saturate the transitions, the fluorescence intensity is a direct measure of the population in a given state.

The rotational distribution of the OH(${}^2\Pi_{3/2}$, $v''=0$) was measured with both the R_1 and Q_1 branches of the ${}^2\Sigma^+ - {}^2\Pi_{3/2}$ transition. Normally, one would expect the same information from both branches. However, because of the inversion symmetry of the Λ doublets, the Q_1 branch probes only the upper component whereas the P_1 or R_1 branch probes only the lower component.⁹

Figure 1 shows the measured fluorescence intensity ratios $Q_1(N)/R_1(N)$ (corresponding to the population inversion) plotted versus N . It is clear that the population is inverted for each N , and this inversion increases with N . Also apparent is the large influence of the initial temperature of the water molecules on the population inversion, as seen in the difference between beam (~ 50 K) versus cell (300 K).

Measurements in saturation give the same results as measurements in the linear regime where we have to divide the fluorescence intensity by the Einstein B coefficients.¹⁰ With the same setup we could quench the Λ doublets by increasing the number of collisions (large delays, high pressure) and obtain $Q_1(4)/R_1(4) = 1$ (statistical limit).

These results are readily explainable when one considers the nature of the transition involved in water, and the dynamical constraints in the dissociation. The ground state of water has the configuration $\dots (1b_2)^2(3a_1)^2(1b_1)^2 : {}^1A_1$ and the HOH angle is $\sim 105^\circ$. The excited state reached at 157 nm has the configuration $\dots (1b_2)^2(3a_1)^2(1b_1)^1 -$

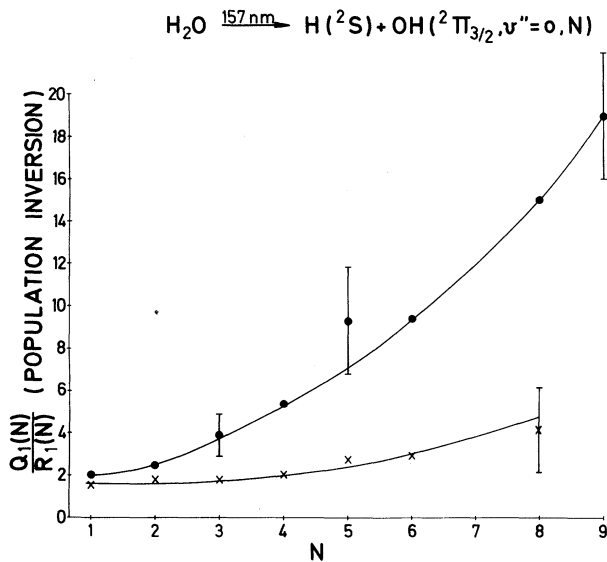


FIG. 1. The observed population inversion in the Λ doublets of OH radicals photolyzed from water in a beam (circles) and in a cell (crosses). The error bars represent one standard deviation from the average at each ratio. The signal-to-noise ratio was best for low rotational states, and decreased with increasing N .

$(3a_1^*)^1: ^1B_1$.⁵ Quantum calculations¹¹ show that water tends to become linear in this configuration, causing a torque on the OH. This is responsible for the OH rotation. Because all forces are directed in the HOH plane, the angular momentum vector of OH (N) will be perpendicular to the HOH plane. Looking closely at the symmetries of the molecular orbitals involved, one finds that an electron is removed from the non-bonding b_1 orbital (essentially the p_x atomic orbital of oxygen which is perpendicular to the HOH plane) and placed in the antibonding a_1^* orbital. As the H atom departs, the OH radical is left with an unpaired electron in a p orbital which remains perpendicular to the HOH plane, i.e., this orbital will be aligned parallel to N . And it is just this configuration (unfilled p lobe parallel to N) which results in the Λ doublet probed by the Q branch of the $^2\Sigma^- \rightarrow ^2\Pi$ transition of OH. The electronic configuration of the ground and excited states of OH are $(1s\sigma)^2(2s\sigma)^2(2p\sigma)^2(2p\pi)^3: ^2\Pi_i$ and $(1s\sigma)^2(2s\sigma)^2(2p\sigma)(2p\pi)^4: ^2\Sigma^+$. The $A-X$ transition takes a $p\sigma$ electron to the unfilled $p\pi$ orbital. Both of these $p\pi$ orbitals are perpendicular to the OH axis, but, for a rotating OH molecule, one of these orbitals is perpendicular to N and the other parallel to N . The interaction of the nuclear rotation with the electronic angular mo-

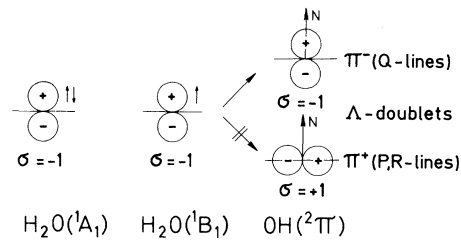


FIG. 2. Simplified picture showing the reflection symmetry of the b_1 molecular orbital involved in the $^1B_1 \rightarrow ^1A_1$ transition of H_2O , and how this correlates with the upper Λ doublet of OH rather than the lower Λ doublet.

mentum ($N \cdot L$) is responsible for splitting the degeneracies of these $p\pi$ orbitals (Λ doubling) and it can be shown that the upper Λ doublet has the unpaired electron parallel to N . The dissociation of water in fact creates such a configuration. This is illustrated in Fig. 2. At the left of the figure one sees the reflection symmetry of the b_1 molecular orbital involved in the $^1B_1 \rightarrow ^1A_1$ transition of water. It can be seen that this orbital only correlates with the upper Λ doublet of OH, and this explains the observed preference for populating this state. For low values of N , the preference for the upper Λ doublet is less pronounced. Also, this preference is much less dramatic when 300-K water is photolyzed. Both of these observations must be due to the initial out-of-plane rotation of the water molecules prior to dissociation. Further work is being done to achieve a cooler H_2O source.

The above discussion is admittedly very qualitative. A more detailed analysis of these results and further measurements of the $^2\Pi_{1/2}$ state as well as the first vibrational state will be published in the near future.¹² The selection of specific Λ doublets by photodissociation may be a general phenomenon and should also be observed for isoelectronic molecules such as H_2S , H_2Se , etc.

The results in themselves seemed to be of importance to settle the question of the interstellar maser. We assume with others that OH is formed in space by the photolysis of water. As a result of the low densities in space it is a reasonable assumption that relaxation of the OH proceeds via infrared emission to the ground state. The selection rules $\Delta J = \pm 1$ and $+\leftrightarrow -$ are such that upper Λ doublets will always decay to upper Λ doublets of the next lower rotational state. The population inversion is maintained in this fashion, resulting in a larger inversion in the ground ro-

tational state. From the rotational state distribution measured, one can calculate the percentage of OH radicals formed in the various rotational states. This, together with the measured population inversions in the beam gives a final ratio of $\sim 4:1$ for the Λ doublets of the (${}^2\Pi_{3/2}$, $v=0$, $J=1.5$) state. Because this inversion is at least two times larger than ratios assumed by others, it clearly shows the feasibility of this simple mechanism.

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Metal-Metal Bonding in Cr-Cr and Mo-Mo Dimers: Another Success of Local Spin-Density Theory

B. Delley, A. J. Freeman, and D. E. Ellis

Physics Department, Northwestern University, Evanston, Illinois 60201

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Self-consistent local-spin-density total-energy calculations for Cr₂ and Mo₂ yield ${}^1\Sigma_g^+$ ground states with dissociation energies and equilibrium bond lengths in excellent agreement with experiment—in marked contrast with the results of a generalized-valence-bond-van der Waals approach, which used 26 512 determinants, and previous local-density efforts. The present results indicate the reliability of local spin-density theory for very inhomogenous systems, when sufficient variational (and symmetry) freedom is included.

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The local density (LD) functional theory¹ is now the most widely used theoretical approach for determining the electronic structure of materials. Its great utility derives from the accurate experimental predictions obtained in systematic and extensive theoretical investigations of the electronic structure and properties of molecules and a wide variety of bulk solids and surfaces. The one striking exception—and indeed perhaps its outstanding failure—lies in the apparent inability of LD theory to describe properly the nature of the metal-metal bonding in such seemingly simple systems as the transition-metal (TM) dimers.² A

recent Letter³ presented potential curves for the Mo₂ and Cr₂ dimers determined from a generalized valence-bond approach that includes correlations for the van der Waals interactions (GVB-vdW). These results, based on a wave function for the ${}^1\Sigma_g^+$ state containing 26 512 Slater determinants involving 18 valence molecular orbitals, disagreed dramatically with those from the earlier LD calculations² and “cast doubt on the efficacy of the local (spin) density approximation in calculations on transition metal systems.”³

The TM dimers pose a severe test for LD theory, which uses an exchange-correlation func-