Simultaneous Determination of Rotational and Translational Temperatures of OH($^2\Pi$) in a Gas Discharge

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We have made simultaneous determination of the rotational and translational temperatures of OH($^2\Pi$) in a water-vapor discharge. These temperatures were determined by measuring the strength and line shape of the absorption lines in the $^2\Pi(v=0)\rightarrow{}^2\Sigma^+(v=0)$ transitions of OH using a cw tunable laser. It was found that the rotational distribution was thermalized, but the corresponding rotational temperature was much lower than the translational temperature. Possible implications of these results are discussed.

The study of OH has been of interest as it relates to the laser emission[1,2] of stellar OH, the airglow[3] in the upper mesosphere, and pollution in the atmosphere.[4] The study of OH as a dissociation product of the water molecule is also of interest since it may yield information on the structure of the excited states of water.[5] This Letter reports some new results which we believe should provide a better understanding of the phenomena mentioned above.

Specifically, we have made the first simultaneous determination of the rotational and translational temperatures of OH($^2\Pi$) in a water-vapor discharge. These temperatures were determined from a measurement of the strength and line shape of the absorption lines in the $^2\Pi(v=0)\rightarrow\Sigma^+(v=0)$ transitions of OH using the second harmonic of the output from a cw tunable dye laser. It was found that the rotational distribution was thermalized, but the corresponding rotational temperature was much colder than the translational temperature. These results demonstrate unequivocally that OH molecules are generated as a dissociation product of water with little rotational excitation, and indicate that the cross section for rotational relaxation of OH($^2\Pi$) in the ground electronic state is at least an order of magnitude smaller than the corresponding cross section of OH($^2\Sigma^+$) in the excited state. In addition, the techniques employed in this study should also be useful in studying the approach to equilibrium in combustion research,[6] and in verifying the calculated transition probabilities[7] of OH.

The experiments were performed with a cw laser source tuned to coincide with the $^2\Pi(v=0)\rightarrow{}^2\Sigma^+(v=0)$ transitions of OH near 3080 Å. This light source was derived as the second harmonic of the output from an argon-laser-pumped dye laser. Fine tuning was accomplished through the use of an intracavity etalon. With the intracavity etalon, the output near 3080 Å was typically 3 μW in power and about 0.072 cm^{-1} in linewidth.

The experimental setup used in our experiments was similar to that reported elsewhere.[8] The second-harmonic beam near 3080 Å was chopped at 83 Hz and split into two beams. One beam was detected with a photomultiplier to provide a reference, and the other was detected by a matching photomultiplier after it traversed at right angles a flowing column of OH generated through dissociation of water vapor in a microwave discharge. The effective absorption path under this arrangement was most likely determined by the lateral diffusion of the gases, and was estimated to be about 11 cm in length. With an appropriate scheme for subtraction and normalization, a change due to absorption of one part in 10^4 in the intensity of the signal beam could be determined.

The location of the microwave cavity upstream from the point of interaction was adjustable between 5 and 30 cm. Over the range of water vapor pressure used, the flow rate was measured to be approximately 300 cm/sec. For a discharge pressure of 1.2 Torr and at a location of 5 cm downstream from the microwave cavity, the OH concentration as deduced from the absorption strength[4] was approximately 8×10^{13} molecules/cm^3. It increased monotonically with the water vapor pressure and decreased slowly with increasing distance from the microwave cavity. At 30 cm, the OH concentration was down by an order of magnitude.

Under conditions of the experiments, OH is generated continuously[9] downstream from the micro-

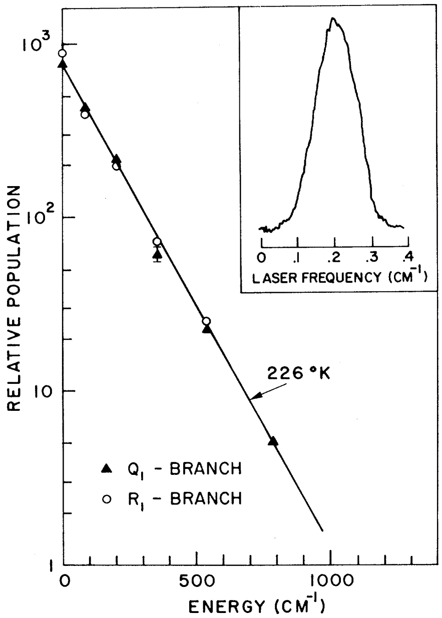

FIG. 1. Plot of relative population in the ground-state rotational levels of OH as a function of the energy of the rotational level. The data were taken at 1.2 Torr of water vapor pressure, and 22 cm downstream from the location of the microwave cavity. Inset: Absorption line shape of the $R_1(3)$ line near 3068.70 Å.

wave cavity. The lifetime of OH is most likely determined by recombination processes involving collisions of OH with HO_2 or the walls of the discharge tube. One estimates that this lifetime should be of the order of 1 msec,[9] and definitely no shorter than 0.1 msec.

In Fig. 1, the relative population of the rotational levels of OH in the ground electronic state is shown as a function of the energy of the rotational levels. It was found to remain unchanged as the location of the microwave cavity was varied. The relative population was obtained as before[6] from the ratio of the measured absorption coefficient to the calculated line transition probability.[7] Results from both R_1- and Q_1-branch transitions are included; they are seen to be consistent with each other well within the overall experimental uncertainty of ± 10%, and indicate a Boltzmann distribution with a rotational temperature of (226 ± 10)°K.

The inset in Fig. 1 shows the absorption line shape of the $R_1(3)$ line observed under the same conditions. This line shape was found to be the same for all the absorption lines investigated. The peak absorption of $R_1(3)$ line corresponded to 16%, and was the highest among the R_1-branch transitions investigated. At these absorption levels, it can be shown that the half-width (full width at half-maximum, FWHM) of the absorption line is practically unaffected by the logarithmic dependence of the observed absorption signal. Since the contribution to linewidth due to pressure broadening is also negligible over the pressure range investigated, the observed width (FWHM) of 0.124 cm^{-1} in the inset should represent the convolution of the laser linewidth and the Doppler width of the absorption line. Upon deconvolution, this Doppler width was found to be 0.1 cm^{-1}. It corresponded to a temperature of 315°K, with a probable error of ± 30°K due mostly to the uncertainty in the measure linewidth of the laser. This temperature should be the translational temperature of the gaseous medium. It is slightly higher than the room temperature of 300°K, but much higher than the deduced rotational temperature of (226 ± 10)°K.

As is evidence by a continuing increase in the linewidth of the absorption transition, the translational temperature was found to increase as the microwave cavity was moved closer to the point of sampling. With the microwave cavity located 5 cm upstream from the point of sampling, the absorption linewidth was found to be 0.13 cm^{-1}, with a corresponding translational temperature of 365°K. This is in contrast with the deduced rotational temperatures which remained unchanged as the location of the microwave cavity was varied.

In an attempt to study the rotational distribution at higher pressures, we have also measured the absorption of OH with the light beam traversing the length of a dc discharge 25 cm in length and operated at pressures up to 20 Torr of water vapor. The translational temperature deduced from the absorption linewidth was found to increase with the pressure of the discharge (Fig. 2). At low pressures, the rotational distribution (Fig. 3) was again found to be "thermalized" at a temperature much lower than the translational temperature; but at higher pressures, deviations from this cold rotational distribution become noticeable. It is seen in Fig. 3 that while the distribution among the low-lying rotational levels remained cold, the distribution among the higher rotational levels correspond to a temperature not much lower than the translational temperature of the medium. This distribution is similar to that observed previously in the emission[10] and absorption[11] spectra of OH.

The results presented above preclude the possibility that the observed cold rotational temperature is an artifact resulting from the inaccuracies

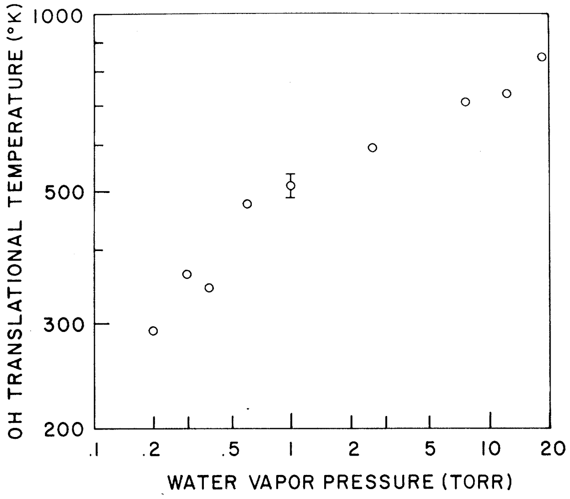

FIG. 2. Plot of the translational temperature deduced from the absorption linewidth of Fig. 1 as a function of the water vapor pressure in a dc discharge.

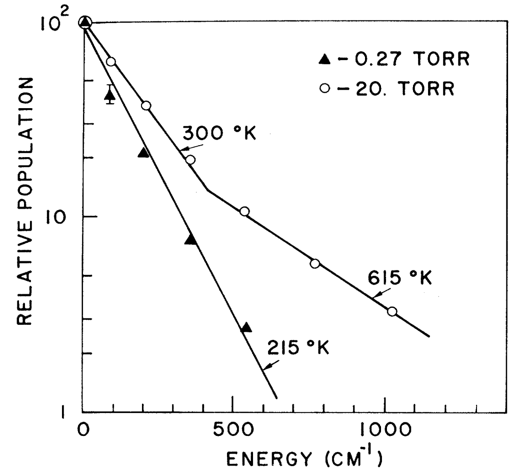

FIG. 3. Plot of the relative rotational population as a function of the energy of the rotational level at two different water vapor pressures in a dc discharge.

in the calculated line transition probabilities[7] or from experimental imperfections.[10,11] The consistency between the results of the R_1- and Q_1-branch transitions makes it unlikely that the rotational distribution is anything but completely thermalized; moreover, the observed difference between the rotational and translational temperatures is too large to be caused by any possible variations in the electronic transition dipole moment.[12] One is thus compelled to conclude that the rotational distribution became thermalized at a temperature lower than the translational temperature of the medium.

The existence of a cold rotational temperature can be explained if OH is originally generated with little rotational energy as discussed previously,[13] and the cross section is too small to allow, during the lifetime of OH, sufficient exchange of energy between the rotation of OH and the translation of other species in the discharge. This being the case, rotational equilibrium could then be established if OH-OH collisions involving nearly resonant rotational transitions are dominant. Rough estimate indicates that this resonant rotational relaxation time[14] should be 0.05 msec or less under our experimental conditions, and thus is much shorter than the 1-msec lifetime of OH discussed earlier. Note that this estimate is consistent with the observation that no change in the rotational distribution could be detected when the location of the microwave cavity was varied, and with the cold rotational temperature indicated in Fig. 3 for the dc discharge at lower pressures.

The existence of a cold rotational temperature under our experimental conditions would indicate an effective cross section of 10^{-16} cm^2 or less for energy exchange between the rotation of OH and the translation of other molecules in a water vapor discharge. In previous studies of rotational relaxation, it is generally noted that this cross section for energy exchange is comparatively small at room temperatures[14] because of the large rotational energy of OH involved, but nonetheless should be of the order[4,15] of 10^{-15} cm^2. However, our value for the cross section refers to OH($^2\Pi$) in the ground electronic state, whereas the latter values were deduced for OH($^2\Sigma^+$) in the excited state. This difference in the cross sections is outside the range of the experimental uncertainties, and thus is a manifestation of the dependence on the electronic (excitation) energy of OH. While this energy dependence is generally known for many molecules, we believe this is the first clear evidence that rotational relaxation times are sufficiently different for OH in the ground and excited electronic states. It follows that relaxation results obtained with OH($^2\Sigma^+$) must be applied with caution when properties[2,3] of OH($^2\Pi$) in the ground electronic states are involved.

The results of Fig. 3 for a dc discharge can also be explained as a lifetime-limited distribution similar to that discussed above. Because of the increased separation between rotational energy levels with increasing rotational quantum number, effective transfer of energy at low pressures would occur through transitions[14] with $\Delta J = \pm 1$ between the lower rotational levels of OH only. At higher pressures, transitions between these lower rotational levels would become more frequent, but their effects on the distribution should be largely offset by the reduced lifetime of OH at increased pressures. This is consistent with the observation in Fig. 3 that the distribution among the lower rotational levels remained relatively cold as the pressure was increased. On the other hand, increased translational temperatures at higher pressures would tend to allow more efficient exchange of energy between the translation of H_2O and the rotation of OH in higher-lying rotational levels, thus increasing the population in these higher-lying rotational levels. Deviations from a thermalized distribution would then result if OH-OH collisions no longer remained dominant throughout the occupied rotational levels. While the effect of temperature inhomogeneity cannot be ruled out completely in our experiments with the dc discharge, this process noted above should at least be partly responsible for the deviations observed in Fig. 3. Further experiments are currently underway to elucidate this process; and the results will be published separately.

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Self-Steepening of the Density Profile of a CO_2-Laser–Produced Plasma

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Interferometric measurements of plasmas produced by CO_2-laser pulses at intensities of 10^{14} W cm^{-2} provide direct evidence for density-profile modification due to radiation pressure.

The application of CO_2 lasers to laser fusion has long suffered from the argument that the longer-wavelength (10.6 μm) radiation of these lasers will be absorbed at plasma densities ($\sim 10^{19}$ cm^{-3}) far removed from the ablation surface. However, this view is altered if the effects of ponderomotive forces[1] in the absorption region are considered. The importance of light pressure in creating gross modification of the plasma density profile, first recognized by Kidder,[2] has recently received considerable attention,[3,4] and its effects demonstrated in computer simulation experiments[5-7] of laser-light absorption. Moreover in the regime where the radiation pressure is much greater than the local plasma pressure ($> 10^{14}$ W cm^{-2} for CO_2 lasers and $> 10^{16}$ W cm^{-2} for Nd:glass lasers), the abosrption should occur at a sharp density discontinuity, the position and shape of which is largely independent of wavelength.[8] In this Letter, we report the first direct measurements made of the self-steepening of the density profile of a laser-produced plasma, through the