

Rotational Energy Distribution of OH Molecules from the $\lambda 3064$ Band

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(Received December 27, 1937)

The rotational energy distribution of the OH molecules has been studied by photometric measurement of the $\lambda 3064$ band. The band excited in the oxy-hydrogen flame and in the copper arc shows a thermal distribution of intensities from which temperatures of 3275°K and 6350°K, respectively, are calculated. The spectrum excited in vacuum tube discharges shows abnormal rotational energy which varies with the pressure of the water vapor in the tube. At current densities used in the experiment, no reduction of rotational energy could be obtained by addition of excess foreign gas.

THE distribution of rotational energy in an emission band spectrum depends upon the conditions of excitation of the emitting molecules, but the distribution does not always indicate the thermal energy or temperature of the gas in which the molecules are excited. Gaviola and Wood¹ were the first to observe that the high rotational temperature derived from the sensitized fluorescence spectrum of HgH was not the true gas temperature. Rieke² has made an extensive study of the abnormal rotation of the HgH molecule in sensitized fluorescence in the presence of N₂ and the more normal rotation when the fluorescence takes place in the presence of OH molecules. Abnormal rotation appears in the negative bands of CO⁺ and the negative N₂ bands excited in a low voltage arc,³ whereas the distribution of energy is much more normal for the same bands in an electrodeless discharge and in the neon transformer glow discharge. Among other bands showing abnormal rotation are the C₂ bands in an acetylene discharge and some He₂ bands. The emission spectrum of the OH molecule excited in an electric discharge also shows an energy distribution greatly in excess of the thermal energy of the emitting gas. Bonhoeffer and Pearson⁴ stated that the abnormal rotation of OH arises from the simultaneous dissociation of H₂O and excitation of OH by electric impact. Oldenberg⁵ showed that the absorption spectrum of OH shows normal rotation and that the

abnormal emission spectrum may be reduced to normal rotation by the addition of large amounts of helium. In some cases, therefore, excess rotational energy can be reduced by collisions during the lifetime of the excited state of the molecules.

The following investigation is a study of the rotational energy distribution of the OH molecules by measurements of the $\lambda 3064$ band excited in electrode and electrodeless discharge tubes in the presence of water vapor alone, and with additions of helium and argon. Measurements have also been made of the band excited in an oxy-hydrogen flame and in a copper arc. Excess rotational energy is found in all cases for the discharge tube spectra, although the amount varies with the conditions in the discharge. On the other hand, the flame and arc spectra both show a normal thermal distribution of rotational energy.

EXPERIMENTAL

Quartz tubes were used for both the electrode and electrodeless discharges. The capillaries were $\frac{1}{4}$ " inside diameter and 2" long. Cylinders of coiled sheet aluminum were used as electrodes and the electrode discharge was excited by a Thordarsen 2.5 kv transformer. The high frequency excitation for the electrodeless discharge was provided by a Sloan⁶ oscillator. The tubes were baked out before being filled with gas. The water vapor pressure in the discharge tubes was controlled by cold alcohol baths surrounding a small sidearm containing a few drops of water.

⁶ D. H. Sloan, R. L. Thornton and F. A. Jenkins, *Rev. Sci. Inst.* **6**, 75 (1935).

¹ E. Gaviola and R. W. Wood, *Phil. Mag.* **6**, 1191 (1928).

² F. F. Rieke, *J. Chem. Phys.* **4**, 513 (1936); **5**, 831 (1937).

³ O. S. Duffendack, R. W. Revans and A. S. Roy, *Phys. Rev.* **45**, 807 (1934).

⁴ K. F. Bonhoeffer and T. G. Pearson, *Zeits. f. physik. Chemie* **14**, 1 (1931).

⁵ O. Oldenberg, *Phys. Rev.* **46**, 210 (1934).

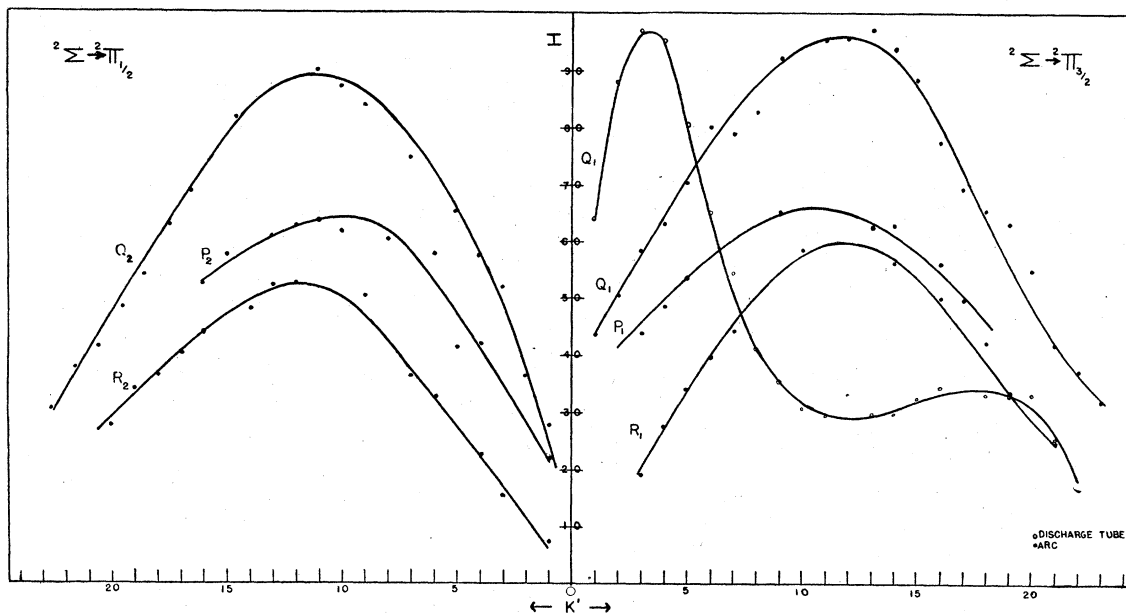


FIG. 1. Intensities of lines of the 6 principal branches of the $\lambda 3064$ band of the OH arc spectrum as a function of the rotational quantum number. One branch of the band excited in a discharge through 2×10^{-2} mm H_2O .

Ordinary distilled water, which was subsequently vacuum distilled several times by means of liquid air, was used. The alcohol baths were made by cooling ethyl alcohol with liquid air to the desired temperature. The baths provided a range of temperatures from -120°C to room temperature. Before each exposure the water vapor was frozen out of the tube by liquid air and the foreign gas added. Then the appropriate alcohol bath replaced the liquid air around the water tube. The foreign gases, helium and argon, were procured spectroscopically pure. A series of spectra was photographed using a constant pressure of helium (7 mm) and varying amounts of water vapor (from 10^{-5} mm to 7 mm) in the electrode discharge tube. A similar series with argon and water vapor in the tube, and a series with water vapor alone in the electrodeless discharge tube was photographed. The latter discharge was used in preference to the inner electrode discharge for the water vapor alone in order to ensure a discharge at very low pressures without overheating the thin electrodes, and to compare the two methods of excitation. Finally a group of photographs was obtained with the electrode discharge through a trace of water vapor and increasing pressures of helium up to

50 cm. In connection with this set of experiments, varying current densities in the discharge tube were also used

The flame spectrum was obtained from the part of an oxy-hydrogen flame just above the cone. The arc spectrum was produced in an arc in air between copper electrodes around which a jet of steam was continuously rising. The arc was really run, therefore, in water vapor at atmospheric pressure contaminated with air.

The photographs were taken in the first order of a 21-foot grating. Eastman 40 plates were used with exposure times of around 5 minutes for the arc, 15 minutes to 2 hours for the discharges, and 1 hour for the flame. The plates were developed in Rodinal. A step weakener was placed directly in front of the photographic plate so that calibration marks were made on the plate at the same time and on some of the same lines whose intensities were to be measured. The transmission of the steps of the weakener as a function of wavelength was measured by means of a quartz photo-cell and a Wynn-Williams amplifier.⁷ The plates were photometered with a Zeiss microphotometer. A calibration curve was obtained for each plate from the photometer trace of the steps

⁷ C. E. Wynn-Williams, *Phil. Mag.* 6, 324 (1928).

of the weakener and the intensities of the lines were then read directly from the curve. A plot of the measured relative intensities of the lines of the six principal branches of the band, excited in the copper arc, against the corresponding rotational quantum numbers, K' , is given in Fig. 1. The intensity distribution in the arc spectrum is thermal. A curve typical of the nonthermal distribution in the discharge tube spectrum is also shown.

RESULTS

If thermal equilibrium exists among the excited molecules, there is a linear relationship according to the Maxwell-Boltzmann theory between the logarithms of I/i and the corresponding rotational term values, where I is the measured intensity of each line and i the theoretical intensity factor. The intensity factors were calculated from formulas of Earls⁸ which are specializations for the ${}^2\Sigma$, ${}^2\Pi$ transitions of the general Hill and Van Vleck⁹ formulas. The term values, $T(K')$, were calculated from the wave numbers for the OH band, $\lambda 3064$, of Heurlinger.¹⁰ Curves were plotted of $\log I/i$ vs. $T(K')$ for each spectrum. Since the curves for each branch of the same band were similar, it was considered necessary in all further work to plot curves only of the Q_1 branch since it was the branch least perturbed by overlapping lines. None of the plots from the discharge tube spectra were straight lines, and all of the curves indicated rotational distributions with energies greater than thermal energies. Fig. 2 shows curves for the water vapor and helium (7 mm) mixtures. There is an excess of energy among the low rotational levels and a more striking excess among high levels. An inhomogeneity of temperature in a carbon arc has been shown by Lochte-Holtgreven and Maeker¹¹ to make the intensities of the low rotational lines in the CN bands too high. Thus temperature inhomogeneity in the discharge could account for the first few high points on the OH curves. The presence of more molecules than expected in the high rotational levels has been found also by Rieke² in the HgH spectrum, and

to a less extent in the same spectrum by Kapuscinski and Eymers.¹² In spite of the non-Maxwellian distribution of energy in the discharge tube spectra, the curves for the different pressures of water vapor are compared by means of the slope in the middle or straight line portion of the curve. In Fig. 2 it is noticeable that the lower the water vapor pressure, the steeper the slope of the curve which indicates that the average rotational energy is lower for lower pressure. Exactly the same effect of variation of average rotational energy with water vapor pressure was found for water vapor and argon (7 mm) and for water vapor alone. Fig. 3 compares data obtained with the same water vapor pressure in the discharge tube for water-helium, water-argon, and water alone. There is agreement among the low rotational levels for the three cases, although the rotational energies differ for the high levels. The argon-water vapor mixtures usually showed the lowest energy for the high rotational levels. From the similarity of the effects with water vapor with and without small amounts of foreign gases, the conclusion

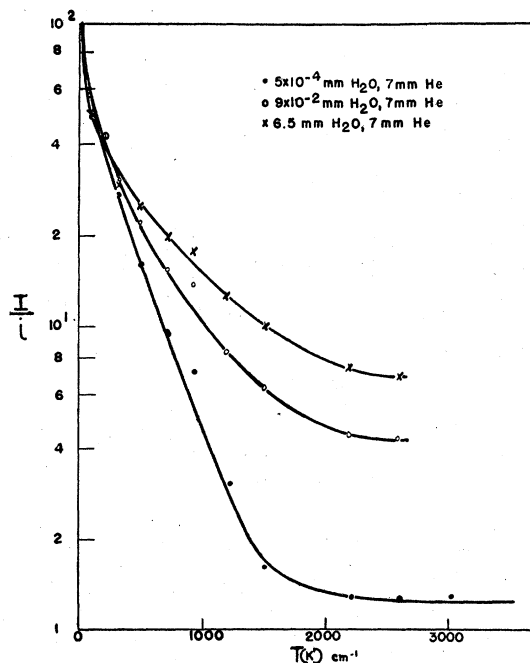


FIG. 2. Rotational term values as a function of $\log I/i$ for constant helium, varying water vapor pressure mixtures.

⁸ L. T. Earls, *Phys. Rev.* **48**, 423 (1935).

⁹ E. Hill and J. H. Van Vleck, *Phys. Rev.* **32**, 250 (1928).

¹⁰ T. Heurlinger, *Dissertation* (Lund, 1918).

¹¹ W. Lochte-Holtgreven and H. Maeker, *Zeits. f. Physik* **105**, 1 (1937).

¹² W. Kapuscinski and J. G. Eymers, *Zeits. f. Physik* **54**, 246 (1929).

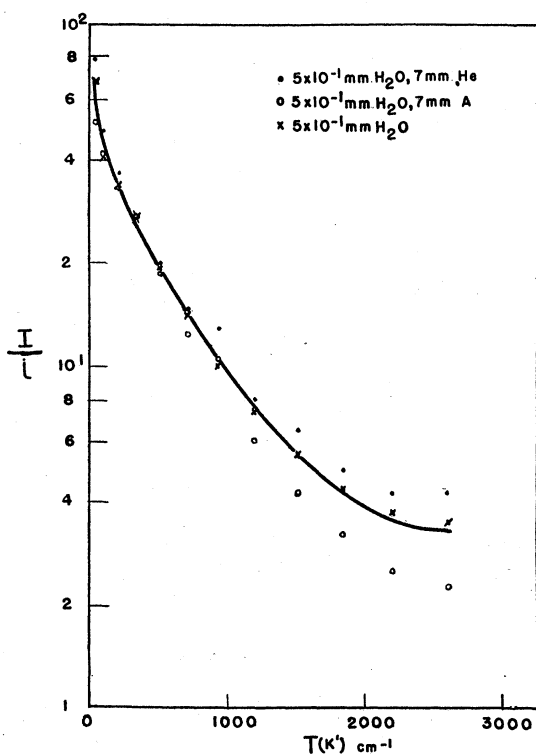


FIG. 3. Rotational term values as a function of $\log I/l$ for constant water vapor pressures in the presence of foreign gases.

may be drawn that the effect of collisions between OH molecules and comparatively small numbers of foreign gas molecules is negligible. The average rotational energy seems to depend only upon the number of OH molecules present in the discharge.

The slope of the middle portion of every curve was determined, and an effective rotational temperature calculated from the slope in order to compare the steepness of the curves. The temperature itself is meaningless because of the absence of thermal equilibrium among the molecules and is used only as a measure of the average rotational energy. In Fig. 4, the effective temperature is plotted as a function of the logarithm of the corresponding water vapor pressure in the discharge. The change in average rotational energy with water vapor pressure was gradual, but not a linear change. Under the conditions of these experiments when the pressure of helium was increased a great deal (up to 50 cm) in the presence of only a trace of water vapor, no change in the rotational distribution was noted. This is in contradiction to the effect of excess foreign gas found by others.^{3, 5} When the current density in the discharge tube was greatly reduced, however, some evidence was obtained from low dispersion spectra that the head of the band was definitely weakened showing a reduction in energy among the molecules. The discharge was so weak that a grating photograph was not feasible. In Oldenberg's photograph of the same effect the head had disappeared completely. Oldenberg did not include data to show whether the distribution of energy in either the pure water or water and helium case was one representing thermal equilibrium.

In the flame spectrum of OH, the expected

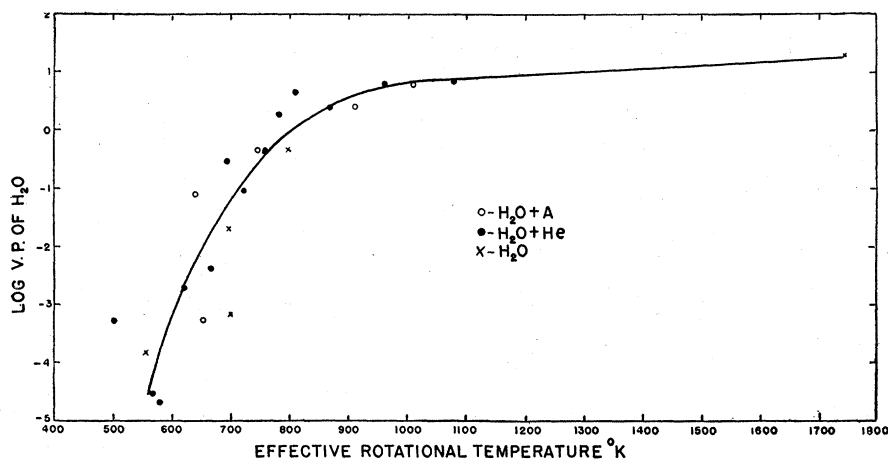


FIG. 4. Effective rotational temperatures as a function of the logarithm of the water vapor pressure in the discharge tube.

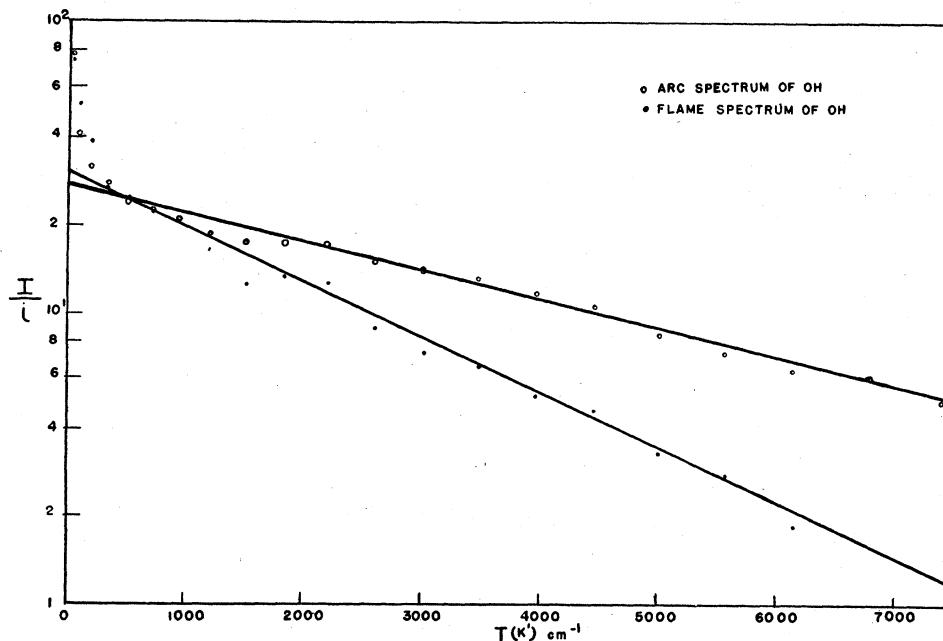


FIG. 5. Rotational term values as a function of $\log I/i$ for the arc and flame excited OH band.

thermal equilibrium among the molecules exists except among these in the lowest rotational levels (Fig. 5). The deviation may be accounted for also as caused by temperature inhomogeneity in the flame. The temperature of the flame was calculated from the slope of the straight line in Fig. 5 as 3275°K, a value in good agreement with the temperature of the oxy-hydrogen flame determined by other methods.

The arc spectrum of OH also showed a Boltzmann distribution of rotational energy with the exception of the temperature inhomogeneity deviation at the low rotational end of the spectrum (Fig. 5). The calculated temperature was 6350°K. The temperature is lower than that found for nitrogen arcs, but the result is consistent with the fact that Jenkins and Ornstein¹³ found that a hydrogen arc was cooler than a nitrogen arc.

DISCUSSION OF RESULTS

The photometric study of the intensity distribution in the OH band, $\lambda 3064$, leads to the

¹³F. A. Jenkins and L. S. Ornstein, Proc. K. Akad. Amsterdam, 35, 10 (1932).

conclusions that the rotational energy of the OH molecules excited in electric discharges may be reduced by decreasing the water vapor pressure in the discharge, or by adding a large excess of foreign gas provided the current density in the discharge is low, but no evidence is found for a Boltzmann distribution even at the highest pressures used. The distribution of rotational energy among the OH molecules in the flame and in the arc is found to represent thermal equilibrium.

Since the process of excitation in an electric discharge is so complicated, it would be advantageous to study the distribution of energy among the OH molecules excited under more simple conditions. Plans have been made, therefore, to measure the rotational energy distribution among the OH molecules excited by sensitized fluorescence.

In conclusion the author wishes to express her thanks and appreciation to Professor F. A. Jenkins who suggested the problem and gave constructive criticism during the course of the research, and to Professor O. Oldenberg for several helpful discussions.