The Absorption Spectrum of Free Hydroxyl Calibrated for a Chemical Test

O. Oldenberg and F. F. Rieke

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The Absorption Spectrum of Free Hydroxyl Calibrated for a Chemical Test

The absorption spectrum has served as a test for free hydroxyl in reacting gases.[1] It obviously serves as a *qualitative test;* it even serves as a *quantitative test in the relative sense* with the help of a certain comparison of intensities of rotational lines. In order to apply it as a *quantitative chemical test* in the *absolute sense* the intensity of the absorption spectrum must be calibrated against a known concentration of hydroxyl. Such a concentration is produced, according to Bonhoeffer and Reichardt,[2] by water vapor thermally dissociated.

The measurement of the absolute intensity of narrow absorption lines presents a difficult spectroscopic problem. This can be carried through by either one of two methods which differ in the background against which the absorption is observed—either a *continuous* or else a *sharp line* emission spectrum may be used as a background. The *continuous* spectrum as a background requires high resolving power of the spectrograph, because the whole contour of the narrow absorption line must be traced; this can be done only with the largest interference spectrographs. On the other hand, the *sharp line spectrum* as a background ("line absorption") requires only a medium size prism spectrograph because only the *total intensity* of a certain line—with and without the absorbing medium—is measured. Therefore "line absorption" is technically a great deal simpler to measure. However, the simplicity of this method is counterbalanced by a serious difficulty in that line absorption is obviously affected by the broadening of both lines—the emission line forming the background and the absorption line to be measured. The case of equal widths of both lines has been treated by Ladenburg and Reiche.[3] Obviously the case of unequal widths is much more complicated.

Avramenko and Kondratjew,[4] in a recent paper, applied an ingenious method to overcome this difficulty. Dealing with an absorption line at a pressure of 760 mm and an emission line at a pressure of 1.5 mm, they are sure of unequal widths of the two lines. On the basis of evidence obtained from atomic spectra they assume that for all pressures above 1 mm, Doppler broadening is negligible, that instead, the width is determined by "collision broadening" and that such a width is proportional to $p/(T)^{\frac{1}{2}}$. Therefore the calibration at $p=760$ mm and $T=1473°K$ can be applied for other values of p and T as long as this type of broadening prevails. Since they had no high dispersion spectrograph at their disposal they had no way of checking this fundamental assumption.

Unfortunately this method fails under the conditions of actual experiment. How wide the discrepancy is will be evident from the following comparison. Under the conditions of the discharge tube (1.5 mm, 300°K), the pressure broadening ought to be at least twice the Doppler broadening in order to make the theory applicable; that is, a pressure broadening of at least 0.02A. Consequently, in the furnace the pressure broadening as computed by the above relation would amount to at least 4.5A. The present authors had an occasion to measure the pressure broadening of OH under the same conditions and found only about 1/120 of this value; therefore Doppler broadening is not negligible but rather is of the same order of magnitude. Because of the smaller width of these lines the absorption effect is more concentrated, and, as a result, the formulae derived by Avramenko and Kondratjew for "weak absorption" are inapplicable for some of their measurements.

These are the reasons why the results of Avramenko and Kondratjew, obtained with "line absorption," differ widely from results obtained by the authors with absorption on a continuous background. The final result of Avramenko and Kondratjew is a probability of the transition $^2\Pi\rightarrow^2\Sigma$ in OH radicals of the same order of magnitude as the probability for the transition $^2P\rightarrow^2S$ in Na atoms; on the other hand, the continuous background leads to a figure smaller by a factor of about 1/1000, a surprisingly small value.

Nevertheless the measurements of Avramenko and Kondratjew are of great interest in another interpretation as follows: In their experiments a line from a low pressure discharge was absorbed by water vapor, thermally dissociated. The present authors, applying the high resolving power of Fabry-Pérot plates, have found that in the discharge the broadening is very small even with a current density of 10 amp./cm². Furthermore, with a 21-foot grating they observed for the furnace (at 1 atmos. and 1473°K) a line width of 0.06A (this includes Doppler broadening and pressure broadening); no shift of the line by pressure takes place. Hence one can consider the narrow emission line as a probe which hits just the center of the absorption line and so indicates the maximum of this line (independent of the width of the emission line as long as it remains narrow; this argument involves the assumption that the emission tube is not operated with too high a current density; the paper published gives only the figures 3000 v a.c., 1.5 kw). With our above value of the line-width, the total absorption is derived from a simple integral. This new interpretation of the measurements of Avramenko and Kondratjew leads to a probability of absorption agreeing rather well with our value mentioned above.

We shall publish our results and their application to the measurement of rate constants of certain hydroxyl reactions in more detail.

O. OLDENBERG

Research Laboratory of Physics,
Harvard University,
Cambridge, Massachusetts,

F. F. RIEKE

Department of Physics,
Johns Hopkins University,
Baltimore, Maryland,
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