Kinetics of OH Radicals Determined by Their Absorption Spectrum IV. Pressure Broadening and the Line Spectrum as Background

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For the measurement of the concentration of OH radicals the intensity of the absorption spectrum is measured more easily with an *emission line* background than with a *continuous* background, provided that the pressure broadening is known. The total broadening of the OH absorption lines at 1473° K and 1 atmos. ($\frac{2}{3}$ O$_2$+$\frac{1}{3}$ H$_2$O) is observed to be 0.58 cm^{-1}; 36 percent of this value is Doppler broadening, the rest is pressure broadening. With this figure, recent intensity measurements of the OH bands by Avramenko and Kondratjew are reinterpreted. The resulting f values of approximately 3×10^{-4} are in reasonable agreement with our previous measurements. The conditions are discussed under which the simple method using the line spectrum as a background is applicable.

I. PROBLEM

IN a preceding paper[1] the probability of transition ("f value") of the OH bands was measured for the purpose of applying the absorption spectrum to a *quantitative* chemical test for free OH radicals in gases. A *continuous spectrum* was used as a background, and for each absorption line the absorption coefficient was measured as a function of wave number throughout the narrow region (a few cm^{-1}) in which the absorption is appreciable. For this method the resolving power of a 21-foot grating is barely sufficient. Technically it would be far simpler to apply the *sharp* OH *band spectrum* in emission as a background and observe the reduction of the total intensity of individual lines when passed through the absorbing gas. This may be measured with a medium-sized quartz spectrograph, which is much more readily available than a large grating spectrograph. Moreover, the total intensity of an emission line which may be photographed with a wide slit requires only one reading on the densitometer, whereas the accurate measurement of the contour of a narrow absorption line is far more difficult. However, this simplified method—using the line spectrum as a background—brings

in a new difficulty in that it requires information regarding the line widths.

With this method Avramenko and Kondratjew[2] determined a certain constant related to the f values (see Section III) and estimated the f values to be much larger than those given subsequently in our paper. We suggest that this discrepancy is due to an incorrect assumption regarding the broadening of the OH lines by the pressure of a foreign gas. Since Avramenko and Kondratjew had no equipment for determining this broadening, they had to rely on an estimate.

Our absorption spectra, published in the paper just mentioned,[1] were taken on a continuous background with high resolving power and give direct evidence of this pressure broadening. In the present paper the broadening is evaluated and applied to a new interpretation of the absorption measurements of the Russian authors; thus an essentially new determination of the f value of the OH absorption bands is obtained.

Although we are mainly interested in the broadening of the lines for the purpose of chemical analysis by absorption spectra, these measurements are of interest also from the purely spectroscopic point of view because very few such measurements on single lines of a molecule are

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[1] O. Oldenberg and F. F. Rieke, J. Chem. Phys. **6**, 439 (1938).

[2] L. Avramenko and V. Kondratjew, Acta Physicochimica **8**, 567 (1937).

known. On the broadening of electronic bands only a short note by Watson and Hull,[3] who investigated AlH bands, is known to us.

II. WIDTH OF THE OH LINES

The width of the individual OH absorption line (portion of line in which the absorption coefficient exceeds 50 percent of the maximum) was measured on the spectra previously described.[1] The line $Q_1(6\frac{1}{2})$, which is free from overlapping, leads to a value 0.58 cm^{-1} at a temperature of 1473°K and a pressure of 1 atmos. ($\frac{2}{3}H_2O + \frac{1}{3}O_2$). As the Doppler broadening at this temperature amounts to 0.21 cm^{-1}, the share contributed by the pressure broadening (assumed to be additive) is 0.37 cm^{-1}. Five other lines, $Q_1(1\frac{1}{2})$ to $Q_1(5\frac{1}{2})$, were measured on the densitometer. As they are overlapped by weaker lines of other branches the resulting contours had to be separated into components. Consequently, the widths derived from these curves are less reliable. All values, however, are well consistent with the width given above. The line width is much more directly derived from the observed spectrum than the f value which was previously reported because the determination of the f value, but not of the line width, requires the computation of the thermal equilibrium. As a matter of fact, one can directly check the figure of the line width on the densitometer trace with reasonable accuracy (see reference 1, Figs. 2 and 3).

The accuracy of our result may, to a certain extent, be affected by the lack of resolving power of the spectrograph.[4] A considerable correction, however, is not to be expected since the observed line width exceeds the theoretical resolving power of the spectrograph by the factor 4. This correction cannot be computed quantitatively because our method of correction applied in the preceding paper (extrapolation to zero absorption) leads to the correct $\int \alpha d\nu$, but leaves width and minimum of intensity uncertain. Because this error can only exaggerate the width, we are certain that the real width is *not greater* than the spectra indicate. On the other hand, it is plausible that the real width is *not considerably smaller* because other lines of atoms or molecules are subject to pressure broadening of *about the same amount* (no lines of a considerably smaller amount) so that we should not expect the OH lines to be exempt from the same effect. Such a broadening effect is theoretically predicted for molecular lines by Margenau[5] as only slightly larger than the effect found for atomic lines. It is clear from our measurement that OH broadened by $H_2O + O_2$ does not provide an example of the anomalously large broadening theoretically predicted by Margenau for special cases.

No pressure *shift* comparable to the pressure *broadening* could be observed at 1 atmosphere. The positions of the absorption lines, both for high pressure (furnace) and low pressure (absorption spectrum of discharge tube after interrupting current), were measured against sharp Al lines emitted together with the hydrogen continuum that formed the background.

A pressure broadening of 0.37 cm^{-1} for OH is comparable to the value 0.24 for the absorption lines of AlH, observed by Watson and Hull,[6] in the atmosphere surrounding a spark discharge. It is also comparable to the broadening of many atomic lines; for instance, the Hg line 2537[7] (0.27 cm^{-1} by 1 atmos. of O_2 at 33°C). Results on the broadening of Hg 2537 and the NaD lines by various other gases—expressed by "effective cross sections"—were summarized by Weisskopf,[8] Margenau and Watson,[9] and, recently, by Schulz.[10]

It is noteworthy that the pressure broadening is of the same order of magnitude for all these lines of *different atoms and molecules* which have no first order Stark effect; they largely follow the Lorentz theory of broadening. Furthermore, the same order of magnitude is found for the broadening of the Hg line 2537 by *different foreign gases* (A, H_2, N_2, O_2, CO_2, H_2O).

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[3] W. W. Watson and G. F. Hull, Jr., Phys. Rev. **49**, 648 (1936).

[4] See the discussion of sources of error in the preceding paper, Section IV.

[5] H. Margenau, Phys. Rev. **49**, 648 (1936).

[6] The conditions are not sharply defined in this absorption experiment because the temperature of the vapor which affects pressure broadening by the factor $1/T^{\frac{1}{2}}$ is rather uncertain in the close neighborhood of the spark.

[7] C. Füchtbauer, G. Joos, and O. Dinkelacker, Ann. d. Physik **71**, 201 (1923).

[8] V. Weisskopf, Physik. Zeits. **34**, 15 (1933).

[9] H. Margenau and W. W. Watson, Rev. Mod. Phys. **8**, 22 (1936).

[10] P. Schulz, Physik. Zeits. **39**, 420 (1938).

III. New Interpretation of the Absorption Measurements of Avramenko and Kondratjew

Avramenko and Kondratjew used the sharp lines of the emission spectrum produced in an electric discharge as a background and measured their loss of total intensity when passing through the absorbing gas. This loss strongly depends on the widths of both lines, emission and absorption. In general, one cannot even represent this loss of intensity along the absorbing path simply by an exponential function since the incident light after passing through a certain length has lost the most absorbable part (core of the line) and continues its path with the less absorbable part (wings of the line). The case of equal widths of both lines was treated by Ladenburg and Reiche.[11] Kondratjew and Ziskin[12] computed approximate formulae for the much more complicated problem of different widths for emission and absorption. By restricting their computation to weak absorption (exponential function approximated by a straight line) they gained the advantage of describing the loss of intensity by an average absorption coefficient. This is proportional to the probability of transition (f value) of the molecule; furthermore, it depends on the widths of both lines.

In Avramenko and Kondratjew's experiment, which is of importance for the determination of the f value, the absorbing medium was water vapor partially dissociated in a furnace. (The concentration of OH can be computed and so provides a calibration of the absorption spectrum of OH.) Pressures and temperatures were known in both the absorbing vapor and the emitting vapor (electric discharge through low pressure). Their great difficulty was the lack of information on the line widths. This was surmounted by the following argument. It was assumed that the widths in both cases (emitting and absorbing vapors) were caused exclusively by the pressure (Lorentz's collision broadening); that is, Doppler broadening was neglected. This approximation, which made the widths proportional to $p/T^{\frac{1}{2}}$, eliminated the line width from the final formula.

Our measurement of the line width (Section

II), which was not accessible to Avramenko and Kondratjew, leads to the conclusion that the approximation just mentioned fails under the conditions of the actual experiments. In what follows, we compute the Doppler broadening from the temperature in the usual way, and determine the pressure broadening by assuming it to be proportional to $p/T^{\frac{1}{2}}$ with the constant of proportionality based on our value for 1473°K and 1 atmos. pressure. In the absorbing vapor used for the calibration (1 atmos. $\frac{2}{3}H_2O+\frac{1}{3}O_2$, 1473°K), it is true that the Doppler broadening (0.21 cm^{-1}) is smaller than the pressure broadening (0.37 cm^{-1}), but it is not negligible. In the remaining cases, in which the absorption was used by Avramenko and Kondratjew to measure an unknown concentration of OH, the Doppler broadening compared to the pressure broadening is in fact the larger of the two. In the discharge tube the Doppler broadening is 0.097 cm^{-1} and the pressure broadening is 0.00016 cm^{-1}. The same objection applies to a lesser extent to the experiment with a flame, reported by the same authors, in which the pressure was 10 mm and the temperature 1000°K. Hence their simplified method, based on a line width proportional to $p/T^{\frac{1}{2}}$, fails.

Nevertheless, their measurements with the line spectrum as a background are of great interest in that they lead to the absolute f values when we apply our line width, reported in Section II, on the basis of the following argument. The line width of 0.097 cm^{-1} in the discharge tube (background) is only one-sixth of the line width of 0.58 in the furnace. Furthermore, no appreciable shift by pressure takes place. Hence we assume as an approximation that the emission line over its whole width is uniformly affected by the coefficient of absorption that belongs to the center of the absorption line; that is, we consider the emission line to be a narrow probe measuring the maximum absorption.

From the values of width (our result) and maximum absorption (measured by Avramenko and Kondratjew) one easily computes the integral absorption coefficient, which is proportional to the number of dispersion electrons per unit volume. When a curve of the type $\alpha_\nu = \alpha_0/[1 + ((\nu - \nu_0)/\delta)^2]$ is assumed for the line contour (Lorentz broadening), where $\alpha_0 =$ maximum ab-

[11] R. Ladenburg and F. Reiche, Ann. d. Physik **42**, 181 (1913).
[12] V. Kondratjew and M. Ziskin, Acta Physiochimica **5**, 301 (1936).

TABLE I. *Comparison of f values. "old": measured with a continuous background and high resolving power; "new": measured with line background and small resolving power, the line width taken from "old" results.*

J	f VALUE (OLD)	f VALUE (NEW)
$4\frac{1}{2}$	2.42×10^{-4}	2.84×10^{-4}
$6\frac{1}{2}$	2.59×10^{-4}	3.45×10^{-4}

sorption coefficient and $2\delta =$ half-value width, the integral absorption coefficient results from $\int \alpha_\nu d\nu = \pi \delta \alpha_0$. The computation of the thermal equilibrium of OH is, of course, the same as in the other measurement published in our previous paper.

This method presupposes that in the discharge tube there is no strong broadening *by current*. Although Avramenko and Kondratjew did not give their current density, it may be assumed that it was not excessive since for their own method they depended on having no extra broadening beyond the effect of a pressure of 1.5 mm.

IV. THE f VALUES

A comparison of our old results (continuous background and high resolving power) with these new results (their measurements of line absorptions and our values of line width) was carried through for the quantum numbers $J = 4\frac{1}{2}$ and $6\frac{1}{2}$ and the temperature of 1473°K. For these figures Avramenko and Kondratjew give the measurements of the "average absorption coefficient" $(\mu l)_{Av}$. To the temperature distribution given in their paper[13] we applied the same equilibrium constants as in our preceding paper in order to make both sets of f values comparable. (The Russian authors applied other values for the equilibrium constant, which they obtained from their own set of measurements.)

The results are given in Table I. The agreement between the "old" and "new" f values confirms the surprisingly small order of magnitude.

The discrepancy between the "new" and "old" f values is presumably due for the most part to incidental errors. However, part of the error may lie in the measurement of the line width since it has not been possible to correct this measurement for lack of resolving power. The true line width may quite possibly be 10 or 20 percent less

[13] H. Zeise, Zeits. f. Electrochem. **43**, 704 (1937).

than our value of 0.58 cm⁻¹. Presumably, the "old" values are more accurate because the correction for lack of resolving power could be applied in their determination (affecting the factor $\int \alpha d\nu$), whereas the same correction (affecting the line width) could not be applied to the "new" value.

V. APPLICABILITY OF THE LINE SPECTRUM AS A BACKGROUND

In order to apply the absorption spectrum as a quantitative test for free radicals, atoms, or molecules, the *line spectrum* as a background has a great technical advantage over the *continuous spectrum* (Section I). This simpler technique is applicable under the following conditions. (a) The total width of the *absorption line* must be known. This figure is given for OH in 1 atmosphere ($\frac{2}{3}H_2O + \frac{1}{3}O_2$) in Section II. For other molecular spectra no accurate figures are available at the present time. Pressure broadening is assumed to be proportional to $p/T^{\frac{1}{2}}$. (b) The *emission line* is restricted by requirements which are more difficult to meet. The simplest case is a width which is small compared to the width of the absorption line (Section IV). Even though the *pressure* and *temperature* in the discharge tube may be low enough, one must still make sure that the *current* does not cause additional broadening. That this is practicable we shall show in a subsequent paper where we shall report on experiments with a line spectrum as background in which Fabry-Pérot plates are applied as a spectrograph which offers still higher resolving power than the second-order of the 21-foot grating. Even with high current density (0.4 amp./mm²) the broadening of the individual OH lines is unexpectedly small. Hence it seems entirely feasible to reduce the current to so low a value that current broadening is negligible. In each case, however, it must be determined whether an increase of current modifies the observed absorption and so indicates an undue current broadening. Since the current broadening can be kept negligibly small and the Doppler broadening is given by a familiar computation, the pressure broadening reported here now makes the simple method which uses the line spectrum as a background suitable for practical application in the quantitative analysis for free OH.