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## The Experimental Determination of the Intensities of Infra-Red Absorption Bands

## I. Theory of the Method\*

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(June 28, 1946)

With spectrographs of available resolving power, the apparent integrated absorption coefficients of infra-red bands usually differ greatly from the true coefficients because the spectrograph yields at each setting a weighted average of the fractional light transmitted in a band of frequencies, whereas what is desired is the unweighted average of the logarithm of the fractional light transmitted. It is shown that true absorption coefficients can be obtained by (a) eliminating the violent fluctuations in intensity with frequency by broadening the rotational lines with a non-absorbing foreign gas and (b) eliminating the error due to the intensity variation of the envelope by extrapolating the apparent integrated absorption coefficient divided by the partial pressure to zero partial pressure of the absorbing gas. These two steps permit vibrational intensities to be measured to a reasonable accuracy even with a spectrograph of low resolving power.

FEW accurate measurements on the intensities of infra-red absorption bands have been published in spite of the utility of such data. Many of the results which have been obtained have been in error by as much as several hundred percent. This error is mainly caused by the lack of adequate resolving power in the spectrographs used. In this paper a method will be described which permits fairly accurate results to be obtained on most substances, even with a spectrograph of low resolving power. This method is primarily useful in handling the vibration-rotation bands of gases whose rotational spacing is not too wide.

## I. DEFINITIONS

It will be assumed that the absorption of strictly monochromatic light is governed by the familiar law

$$I = I_0 \exp(-\alpha pL), \quad (1)$$

where  $I$  is the light transmitted by a cell of length  $L$  containing a gas at pressure  $p$ , and  $I_0$  is the incident intensity.  $\alpha$  is the absorption coefficient divided by the pressure and is assumed to be independent of  $p$  and  $L$  but dependent on the frequency.<sup>1</sup> The quantity which

\* Much of the material in this paper is taken from a thesis by A. J. Wells, submitted to the Department of Chemistry, Harvard University, in May, 1941. A short note was published in *J. Chem. Phys.* 9, 659 (1941).

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<sup>1</sup> Actually  $\alpha$  is not strictly independent of  $p$  due to self-broadening, but this does not affect the later arguments, when the total pressure, including that of a foreign gas, is held constant.

is desired for comparison with theory is the integrated absorption coefficient for unit pressure

$$A = \int \alpha d\nu = (1/pL) \int \ln(I_0/I) d\nu, \quad (2)$$

where the integration is carried out over the frequency range covered by a given band. If a spectrograph of infinite resolving power were available,  $I_0/I$  could be measured directly and there would be no problem.

No actual spectrograph measures  $I$  or  $I_0$  for a single frequency but instead measures the integral of the intensity in a range of frequencies. Let  $T$  be the apparent intensity registered by the instrument at a setting  $\nu'$  (representing the central frequency admitted by the finite slit). Then

$$T = \int I(\nu)g(\nu, \nu') d\nu, \quad (3)$$

where  $g(\nu, \nu')$  is the fraction of the light of actual frequency  $\nu$  which is registered by the instrument when its setting is  $\nu'$ . The integration is carried out over all values of  $\nu$  for which  $g(\nu, \nu') \neq 0$ . Since  $g$  will diminish rapidly outside of a narrow band centered at  $\nu'$ , the limits of integration can be extended to  $\pm \infty$  without harm. A similar expression holds for  $T_0$  in which  $I_0$  replaces  $I$ . It is convenient to define an apparent absorption coefficient  $p\beta$  for frequency  $\nu'$  by the equation

$$p\beta = (1/L) \ln(T_0/T), \quad (4)$$

and, for each band, an integrated apparent absorption coefficient  $B$  for unit pressure

$$B = \int \beta d\nu' = (1/pL) \int \ln (T_0/T) d\nu'. \quad (5)$$

$T$  and  $B$  are measurable quantities from which  $A$  is to be obtained.

## II. EXTRAPOLATION THEOREM

It is desired to prove that

$$\lim_{pL \rightarrow 0} B = A.$$

To do so examine the difference

$$\begin{aligned} A - B &= (1/pL) \int \ln (TI_0/T_0I) d\nu' \\ &= (1/pL) \int \ln \frac{\int f(\nu)g(\nu, \nu') d\nu}{f(\nu') \int g(\nu, \nu') d\nu} d\nu', \quad (6) \end{aligned}$$

where

$$f(\nu) = \exp(-\alpha pL) = I/I_0, \quad (7)$$

and  $I_0$  has been assumed to be constant over a slit width.<sup>2</sup>

If  $f$  were constant over a slit width, it could be removed from the inner integral and the expression would vanish, so that, for resolving power large compared with the variations of  $\exp(-\alpha pL)$ ,  $A$  and  $B$  are equal. But in practice this exponential will go rapidly from nearly zero to nearly one through each rotation line, if there is enough gas to make the average absorption appreciable. Under these conditions  $A$  and  $B$  will diverge widely.

Now consider the limit as  $pL \rightarrow 0$ . Differentiate the integral and the quantity  $pL$  in (6). The result is, after a few steps,

$$\begin{aligned} \lim (A - B) &= \lim \int \left\{ \alpha - \frac{\int \alpha f g d\nu}{\int f g d\nu} \right\} d\nu' \\ &= \int \left\{ \alpha - \frac{\int \alpha g d\nu}{\int g d\nu} \right\} d\nu', \quad (8) \end{aligned}$$

since  $f \rightarrow 1$  in the limit.

<sup>2</sup> This assumption may break down in regions of absorption by water vapor or carbon dioxide in the atmosphere unless these materials are excluded from the light path.

If this expression vanishes, the desired theorem is proved. But it will vanish if the absorption coefficient  $\alpha$  is constant over a slit width, a much less stringent condition than that its exponential be considered constant. Moreover, under certain conditions this expression will vanish regardless of the variations of  $\alpha$ . Thus if  $g(\nu, \nu') = g(\nu - \nu')$  only, i.e., if the resolving power is constant over the width of the band, and if  $g(\nu - \nu') = g(\nu' - \nu)$ , then

$$\int g(\nu - \nu') d\nu = \int g(\nu - \nu') d(\nu - \nu') = G, \quad (9)$$

which is independent of  $\nu'$ . Also

$$\int \int \alpha g d\nu d\nu' = \int \alpha \int g d\nu' d\nu = G \int \alpha d\nu, \quad (10)$$

so the expression in Eq. (8) will reduce to<sup>3</sup>

$$\int \alpha d\nu' - \int \alpha d\nu = 0. \quad (11)$$

Consequently, if the incident intensity  $I_0$  does not vary rapidly over a slit width and if either the resolving power is high compared with the variations in  $\alpha$  or the resolving power does not change much over the band,

$$\lim_{pL \rightarrow 0} B = A. \quad (12)$$

Therefore by measuring  $B$  at a series of values of  $pL$  (either by changing  $p$  or  $L$ ) and extrapolating to zero  $pL$ , the true integrated absorption  $A$  can be found.

## III. PRESSURE BROADENING

In practice the fluctuations of  $f = \exp(-\alpha pL)$  will be very extreme on passing through each line of the rotational fine structure. Consequently, where such fine structure exists, it might be necessary to carry the measurements to impractically low values of  $pL$  before a good limit could be estimated. To remedy this, the rotational fine structure can be eliminated by pressure broadening with the use of a sufficiently high pressure of a non-absorbing foreign gas, as was done by Bartholomé<sup>4</sup> for HCl.

<sup>3</sup> A similar argument has been used by D. M. Dennison, Phys. Rev. **31**, 503 (1928), for a slightly different purpose.

<sup>4</sup> E. Bartholomé, Zeits. f. physik. Chemie **B23**, 131 (1933).

With spectrographs of high resolving power, the use of a foreign gas to eliminate the rotational fine structure may be sufficient to make  $B$  essentially equal to  $A$  without extrapolation but for poorer spectrographs the variation of  $f = \exp(-\alpha pL)$  over the band envelope may still be sufficiently great to cause very large differences between  $A$  and  $B$ , as was pointed out by Kemble.<sup>5</sup> The extrapolation procedure then takes care of this.

#### IV. ABSORPTION AREAS

Bourgin,<sup>6</sup> in studying the intensity of individual HCl rotation-vibration lines, extrapolated the integral ("absorption area")

$$pLC = \int [(T_0 - T)/T_0] d\nu', \quad (13)$$

instead of  $B$ . By expansion of the logarithm in  $B$ , one gets

$$B = (1/pL) \int (x + \frac{1}{2}x^2 + \dots) d\nu', \quad (14)$$

where

$$x = (T_0 - T)/T_0, \quad (15)$$

so that in the limit  $B$  and  $C$  are also equal. However,  $B$  is always larger than  $C$  and various arguments indicate that  $B$  is normally less than  $A$  so that  $B$  extrapolates to  $A$  more conveniently and rapidly than  $C$ . As shown by Dennison,<sup>3</sup>  $C$  is independent of the resolving power whereas  $B$  is not (at finite values of  $pL$ ). Therefore the use of a better spectrograph assists the extrapolation when  $B$  is used but does not with  $C$ .

#### V. EFFECT OF STRAY LIGHT

In most spectrographs light of a frequency quite foreign to that being studied enters the detecting instrument, which if not taken into consideration will falsify the results. If the amount of stray is known, it can be corrected for, either by subtracting the stray intensity  $S$  from each observation  $T'$  or by correcting  $B$  after integration. If the stray is greater than about 10 percent of the total intensity  $T_0$ , it is more accurate to correct each observation.

Let  $T_0 = T'_0 - S$  and  $T = T' - S$  so that the uncorrected integral  $B'$  is

$$\begin{aligned} B' &= (1/pL) \int \ln [T'_0/T'] d\nu' \\ &= (1/pL) \int \ln [(T_0 + S)/(T + S)] d\nu'. \end{aligned}$$

If  $S$  is independent of  $pL$ , then by differentiation one gets

$$\begin{aligned} \text{Lim } B' &= -\text{Lim} \int [1/(T + S)] [dT/d(pL)] d\nu' \\ &= -\text{Lim} \int \frac{dT/d(pL)}{[1 + (S/T_0)] T_0} d\nu' \\ &= (1/[1 + (S/T_0)]) \text{Lim } B, \end{aligned}$$

if  $1 + (S/T_0)$  is constant over the band. If the stray is not too large, it should therefore not interfere with the accuracy of the extrapolation method, since it can be corrected for. It should be noted, however, that the stray may also be absorbed by the material under study, thus introducing a further source of error.

#### VI. SUMMARY OF METHOD

The above considerations show that it should be possible under proper conditions to obtain values of the intensity of an infra-red vibrational absorption band (integrated over the various rotational lines) by measuring the integrated apparent absorption coefficient for unit pressure  $B$  (see Eq. (5)) at a series of partial pressures of the absorbing gas and extrapolating this quantity to zero partial pressure. The rotational fine structure should be eliminated by means of a sufficiently high pressure of some suitable non-absorbing gas. The extrapolated value of  $B$  should then equal the true integrated absorption coefficient at unit pressure,  $A$ .

Care needs to be taken that the presence of atmospheric absorption bands does not cause the intensity of the incident beam to vary rapidly in the frequency band admitted by the slit and also that the resolving power of the instrument does not vary excessively from one end of a band to the other. Correction needs also to be made for stray light.

<sup>5</sup> E. C. Kemble, J. Chem. Phys. **3**, 316 (1935).

<sup>6</sup> D. G. Bourgin, Phys. Rev. **29**, 794 (1927).