[CONTRIBUTION FROM THE DIVISION OF CHEMISTRY OF THE NATIONAL RESEARCH COUNCIL OF CANADA]

Intensities and Shapes of Infrared Absorption Bands of Substances in the Liquid Phase[1a]

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The factors influencing the shapes of infrared absorption bands in liquids are discussed. It is concluded that the true shape of a single absorption band of a liquid may be represented by a Lorentz curve. The effect of scanning a Lorentz curve with a triangular slit function has been computed and relationships established between the true and apparent peak intensities, the half-band widths and the slit widths. Three methods are described for the determination of the true integrated absorption intensity of an infrared absorption band of a liquid from experimental data obtained with a spectrometer of moderate resolving power. One method involves direct integration of the Lorentz equation, a correction factor being applied for the use of finite slit widths. The other methods are extensions of the extrapolation procedures used by Bourgin and by Wilson and Wells for gases. Assuming a Lorentz curve for the true band shape and using a triangular slit function, it is shown that linear extrapolations may be obtained by plotting suitable functions. The correction factor for finite slit widths in the Wilson–Wells method is found to be small (~5%). A more important factor applicable to both methods is the correction (~10%) for the residual area under the "wings" of the absorption band. Tables are given to assist the experimental application of these methods.

In recent years considerable attention has been given to the interpretation of the infrared absorption spectra of complex organic compounds. Interest has centered principally on attempts to associate absorption bands at specific frequencies with the presence of certain chemical groups in the molecule.[2–7]

In an investigation of the carbonyl stretching vibrations of steroids[8,9] it was found that different carbonyl groups may give rise to absorption bands at the same position, in which case the type of absorbing group cannot be characterized from the position of the absorption maximum alone.

Measurement of the intensity of the absorption might provide additional information about the nature of the absorbing groups. The determination of the intensities of infrared absorption bands of liquids and solutions has received comparatively little attention and the present investigation was undertaken to establish convenient methods for the accurate evaluation of infrared band intensities. The application to the specific problem of the steroid carbonyl bands is discussed in the following paper.[10]

Expressions for the Representation of Band Intensity

If the well known absorption law

$$I_\nu = I_{0\nu}e^{-\alpha_\nu cl} \qquad (1)$$

where $I_{0\nu}$ and I_ν are the incident and transmitted intensities of *monochromatic* radiation of frequency ν; α_ν is the adsorption coefficient for frequency ν, c is the concentration of the solute in moles per liter, and l is the cell length in cm.

is assumed to hold for liquids and solutions, the *true integrated absorption intensity* (A) of a band is defined as

$$A = \int \alpha_\nu \mathrm{d}\nu = \frac{1}{cl}\int \log_e \left(\frac{I_0}{I}\right)_\nu \mathrm{d}\nu \qquad (2)$$

the integral being measured over the limits of the absorption band.

In practice, due to the use of finite slit widths,[11] the radiation is not monochromatic and the quantity measured is the *apparent integrated absorption intensity* (B) given by

$$B = \frac{1}{cl}\int \log_e \left(\frac{T_0}{T}\right)_\nu \mathrm{d}\nu \qquad (3)$$

where $T_{0\nu}$ and T_ν are the *apparent* intensities of the incident and transmitted radiation when the spectrometer is set at frequency ν.

Another quantity, commonly used in *ultraviolet* spectrophotometry as a measure of band intensity, is the *true molecular extinction coefficient*, $E^{\mathrm{t}}_{\max}$, at the absorption maximum, $\nu_{\max}$, where

$$E^{\mathrm{t}}_{\max} = \frac{1}{cl}\log_{10}\left(\frac{I_0}{I}\right)_{\nu_{\max}} \qquad (4)$$

the logarithms being expressed to the base 10.

Again, due to the use of finite slit widths, the quantity measured experimentally is the *apparent molecular extinction coefficient*, $E^{\mathrm{a}}_{\max}$, at the absorption maximum where

$$E^{\mathrm{a}}_{\max} = \frac{1}{cl}\log_{10}\left(\frac{T_0}{T}\right)_{\nu_{\max}} \qquad (5)$$

With prism instruments at present in use in the infrared, the spectral slit widths are of the same order as the widths of absorption bands of liquids and solids. Under these conditions the band intensities determined experimentally are not true physical constants of the absorbing molecule, but depend on the instrumental conditions employed. It is shown in this paper that with a slit width equal to one-half the true width of the absorption band, the true and apparent molecular extinction coefficients differ by ~20%. The difference in the integrated intensity measurements, however, is only ~2-3%, the decrease in peak intensity produced by the finite slit width being roughly compensated by an increase in band width.

Apparent integrated intensity measurements have been made by Fox and Martin[12] on some C–H bands in the region

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[1] (a) Published as Contribution No. 2565 from the Laboratories of the National Research Council of Canada. (b) Now with the Division of Physics, National Research Council of Canada.

[2] R. B. Barnes, U. Liddel and V. Z. Williams, *Ind. Eng. Chem., Anal. Ed.*, **15**, 659 (1943).

[3] Faraday Society Symposium, *Trans. Faraday Soc.*, **41**, 171 (1945).

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[7] N. B. Colthup, *J. Optical Soc. Am.*, **40**, 397 (1950).

[8] R. N. Jones and K. Dobriner, *Vitamins and Hormones*, **7**, 293 (1949).

[9] R. N. Jones, P. Humphries and K. Dobriner, THIS JOURNAL, **72**, 956 (1950), and earlier publications.

[10] R. N. Jones, D. A. Ramsay, D. S. Keir and K. Dobriner, *ibid.*, **74**, 80 (1952).

[11] E. B. Wilson, Jr., and A. J. Wells, *J. Chem. Phys.*, **14**, 578 (1946).

[12] J. J. Fox and A. E. Martin, *Proc. Roy. Soc. (London)*, **A162**, 417 (1937).

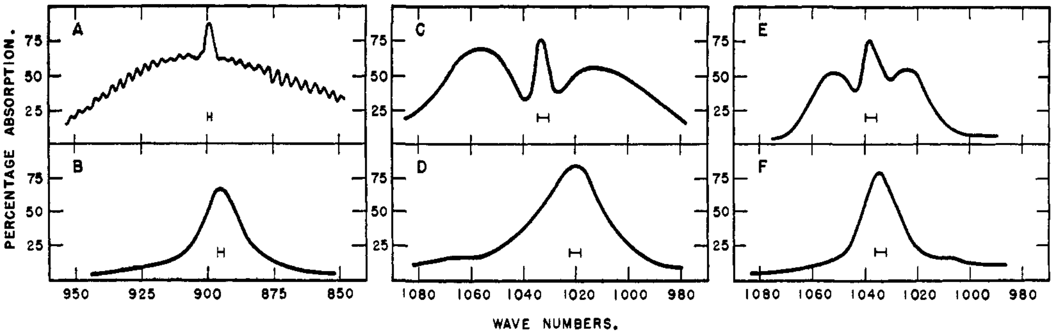

Fig. 1.—Comparison of the shapes of some infrared absorption bands in the vapor and in the liquid phase: A, *trans*-dichloroethylene vapor, path length 10 cm., pressure 30 mm.; B, *trans*-dichloroethylene liquid, 10% solution in CS$_2$, 0.025-mm. cell; C, methyl alcohol vapor, path length 10 cm., pressure 10 mm.; D, methyl alcohol liquid, 0.2% solution in CS$_2$, 1-mm. cell; E, benzene vapor, path length 10 cm.; pressure 80 mm.; F, benzene liquid, 15% solution in CCl$_4$, 0.1-mm. cell.

of 3 μ, by Wulf, Liddel and Hendricks[13] for O–H and N–H bands, by Richards and Burton[14] for N–H and C=O bands and by Francis[15] who examined several characteristic absorption bands of aliphatic hydrocarbons. In many cases it was possible to assign characteristic intensity ranges to various types of absorbing groups. In two of the investigations[12,15] grating spectrometers were used and the corrections for finite slit widths were very small. Apparent molecular extinction coefficients have been employed by several investigators[16–19] for survey work, and, provided the instrumental conditions were maintained approximately constant, characteristic ranges of intensity could be assigned to certain types of absorbing groups.

Discussion of Band Shapes

Since one of the main difficulties encountered in the measurement of true intensities of absorption bands lies in the use of finite slit widths, a knowledge of the true band shape is of particular interest, since the effect of slit width on band shape may then be computed for various slit functions. Furthermore, it also becomes possible to extend the methods of Bourgin[20] and of Wilson and Wells[11] for the determination of true integrated absorption intensities from experimental absorption curves (see later).

For these reasons an investigation of the shapes of infrared absorption bands of liquids and solutions was carried out and an attempt made to find a general empirical or semi-empirical equation to express the *true* shape of a single absorption band.

In examining this problem, three factors were considered which may be expected to exert a predominant influence on band shapes.

I. The Significance of Vibration–Rotation Structure in the Liquid State and in Solution.—It is important to consider whether infrared absorption bands in liquids show any vibration–structure or correspond merely to broadened vibrational bands. The only well-established case of rotational structure in the liquid state[21] is that of hydrogen for which two rotational lines have been observed in the Raman spectrum of the liquid.[22] With larger molecules the rotational lines in the gas phase are more closely spaced and the broadening of the lines on passing to the liquid state might permit only the appearance of a rotational contour. A comparison of the shapes of some infrared bands in the vapor phase and in the liquid phase however, shows that in general this is not the case, the rotational contributions present in the vapor phase spectra being absent from the liquid phase spectra (see Fig. 1). Other examples may be found in the literature to support this conclusion.

II. Factors Contributing to the Widths of Absorption Bands.—Since infrared absorption bands in liquids and solutions appear to correspond to broadened vibrational bands, the various factors which might contribute to the broadening will now be considered. These are (i) natural line width, (ii) Doppler broadening, (iii) perturbations by neighboring molecules. General discussions of these effects have been given by Margenau and Watson,[23] Tolansky,[24] White[25] and others, hence the present discussion will be limited to a consideration of the magnitudes of these factors and of the effects on band shape which they may be expected to produce.[26]

The half-intensity widths of infrared absorption bands in liquids[10] are generally ~ 10 cm.$^{-1}$,[27] hence we may neglect the contributions from natural line width and Doppler broadening[25] which may be shown to be $\sim 10^{-6}$ cm.$^{-1}$ and $\sim 10^{-3}$ cm.$^{-1}$, respectively. The principal factor producing broadening in liquids is undoubtedly perturbation by neighboring molecules and although it is not pos-

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(13) U. Liddel and O. R. Wulf, THIS JOURNAL, **55**, 3574 (1933); O. R. Wulf and U. Liddel, *ibid.*, **57**, 1464 (1935); O. R. Wulf, U. Liddel and S. B. Hendricks, *ibid.*, **58**, 2287 (1936).

(14) R. E. Richards and W. R. Burton, *Trans. Faraday Soc.*, **45**, 874 (1949).

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(16) F. W. Rose, Jr., *J. Research Natl. Bur. Standards*, **20**, 129 (1938).

(17) J. A. Anderson, Jr., and W. D. Seyfried, *Anal. Chem.*, **20**, 998 (1948).

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(20) D. G. Bourgin, *Phys. Rev.*, **29**, 794 (1927).

(21) See G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Company, New York, N. Y., 1945, p. 531.

(22) J. C. McLennan and J. H. McLeod, *Nature*, **123**, 160 (1929).

(23) H. Margenau and W. W. Watson, *Rev. Modern Phys.*, **8**, 22 (1936).

(24) S. Tolansky, "High Resolution Spectroscopy," Methuen and Co., Ltd., London, 1947, Ch. 1.

(25) H. E. White, "Introduction to Atomic Spectra," McGraw-Hill Book Co., Inc., New York, N. Y., 1934, Ch. XXI.

(26) The author wishes to acknowledge helpful correspondence with Dr. D. Z. Robinson.

(27) In certain exceptional cases, *e.g.*, hydrogen bonded OH bands, (J. J. Fox and A. E. Martin, *Proc. Roy. Soc.* (*London*), **A162**, 419 (1937)), band widths ~ 100 cm.$^{-1}$ may be found.

sible to make detailed calculations,[28] it is interesting to note that if a statistical distribution of perturbations is assumed, the shape of the broadened band may be represented by the equation[29]

$$\log_e \left(\frac{I_0}{I}\right)_\nu = \frac{a}{(\nu - \nu_0)^2 + b^2} \qquad (6)$$

where ν_0 is the frequency of the band center, and a and b are constants.

A preliminary investigation indicated that the shapes of many infrared absorption bands in liquids could be fitted approximately by an equation of this type, hence it was decided to investigate the effect of finite resolving power on this particular band shape.

III. Effect of Finite Resolving Power.—The energy from the exit slit of a spectrometer set at a frequency ν' is not strictly monochromatic but may be expressed by an energy distribution function $\rho(\nu, \nu')$.[30] If a "true" absorption band given by equation (6) is scanned by a spectrometer of finite resolving power, the "apparent" absorption band obtained is given by the equation

$$\left(\frac{T}{T_0}\right)_{\nu'} = \frac{\int \rho(\nu,\nu') \exp \frac{-a}{(\nu - \nu_0)^2 + b^2} \, d\nu}{\int \rho(\nu,\nu') \, d\nu} \qquad (7)$$

If it is assumed that (i) the intensity of the incident radiation is constant over the slit width, (ii) the dispersion is constant over the exit slit, and (iii) the widths of the entrance and exit slits are equal, then, for a spectrometer with perfect optics, the slit function $\rho(\nu, \nu')$ may be represented by a triangle whose base length is equal to twice the slit width, s, (Fig. 2).[31] This condition does not hold for a prism spectrometer, but provided the resolution of the prism in wave numbers is small compared with the mechanical widths of the slits in wave numbers, the energy distribution may be represented to a first aproximation by a triangle with a half energy spectral slit width given[32] by

$$s(\text{cm.}^{-1}) = \frac{\nu^2(1 - n^2 \sin^2\alpha/2)^{1/2}}{8 \sin \alpha/2 \times \frac{dn}{d\lambda}} \frac{s_1 + s_2}{f} + F(s) \frac{\nu}{2b \frac{dn}{d\lambda}} \qquad (8)$$

where ν is the frequency in cm.$^{-1}$, n is the refractive index of the prism at frequency, ν, α is the prism angle, $dn/d\lambda$ is the dispersion of the prism material in cm.$^{-1}$, s_1, s_2 are the slit widths in cm., f is the focal length of the camera in cm., and b the prism base in cm. F(s) is a function varying from about 0.9 for $s = 0$ to 0.5 for $s = \nu/2b \, dn/d\lambda$. The first term represents the contribution from the finite slits and the second term the contribution from the finite resolving power of the prism.

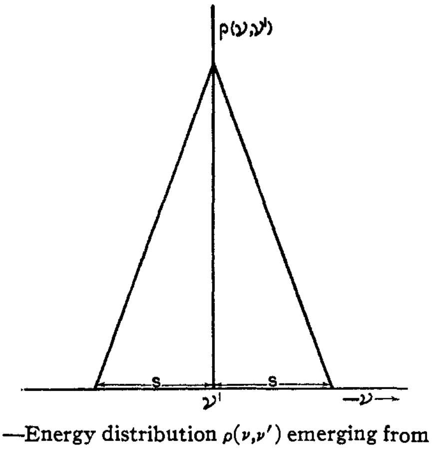
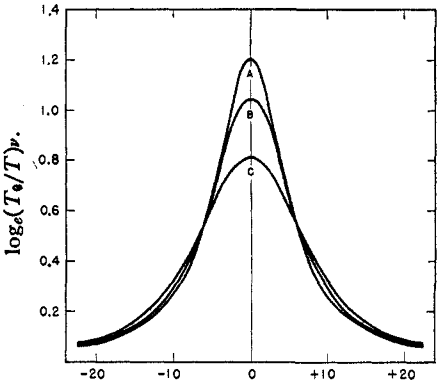


Fig. 2.—Energy distribution $\rho(\nu,\nu')$ emerging from the exit slit of a spectrometer set at frequency ν', assuming perfect optics and entrance and exit slit widths equal to s.

Computation of Apparent Absorption Curves.—Equation 7 was evaluated by numerical integration, using a triangular slit function, for various values of a, b and the slit width s. A typical family of curves is shown in Fig. 3. These "apparent" band shapes could not be expressed by any simple equation,[33] hence it was decided to characterize them by their apparent peak intensity [$\log_e(T_0/T)\nu_{\max}$] and apparent half-intensity width ($\Delta\nu^a_{1/2}$), and to relate these quantities to the true peak intensity [$\log_e(I_0/I)\nu_{\max}$], the true half-intensity width ($\Delta\nu^t_{1/2}$) and the slit width, s. For convenience the ratios $\frac{\log_e(I_0/I)\nu_{\max}}{\log_e(T_0/T)\nu_{\max}}$ and $\Delta\nu^a_{1/2}/\Delta\nu^t_{1/2}$ were calculated as functions of the apparent peak intensity and of the ratio of the slit width, s, to the apparent half band width $\Delta\nu^a_{1/2}$, and are given in Tables I and II. These tables extend to $s/\Delta\nu^a_{1/2} = 0.65$ which is approxi-



Wave numbers from band center.

Fig. 3.—Family of computed curves for various ratios of the slit width to the true half-intensity band width: A, $i/\Delta\nu^t{}_{1/2} = 0$; B, $s/\Delta\nu^t{}_{1/2} = 0.5$; C, $s/\Delta\nu^t{}_{1/2} = 1.0$.

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(28) If the kinetic expression for the half-intensity width, $\Delta\nu^1/_2$, of a collision broadened line in the gas phase,[25] *viz.*, $\Delta\nu^1/_2 = 4Na^2\rho \sqrt{\frac{RT}{\pi M}}$, where N = Avogadro no., a = collision diameter, ρ = density, R = gas constant, T = absolute temperature, M = molecular weight, is applied to the liquid state and reasonable values substituted, *e.g.*, a = 5 Å., ρ = 1 g./ml., T = 300°K., M = 100, values for $\Delta\nu^1/_2$ of the order of 10 cm.$^{-1}$ are obtained.

(29) This equation is referred to as a Lorentz curve in this paper.

(30) This function is referred to throughout this paper as the slit function.

(31) D. M. Dennison, *Phys. Rev.*, **31**, 503 (1928).

(32) V. Z. Williams, *Rev. Sci. Instruments*, **19**, 151 (1948).

(33) An equation of type (6) could be fitted to the central region or to the "wings" of an apparent absorption band but not to both together. Richards and Burton[14] recently attempted to fit various functions to some experimentally determined band shapes and found that a Lorentz curve was not satisfactory. They found that a simple-error curve fitted their curves within experimental error. In our experience an error curve can be made to fit the central regions of an experimental band but falls too rapidly to account satisfactorily for the absorption in the "wings" of the band.

TABLE I

VALUES OF $\log_e(I_0/I)_{\nu_{\max}}/\log_e(T_0/T)_{\nu_{\max}}$ IN TERMS OF THE APPARENT PEAK INTENSITY, $\log_e(T_0/T)_{\nu_{\max}}$, AND OF THE RATIO OF THE SLIT WIDTH TO THE APPARENT HALF-INTENSITY BAND WIDTH, $s/\Delta\nu^a_{1/2}$

$\log_e\left(\frac{T_0}{T}\right)_{\nu_{\max}}$	$\log_e\left(\frac{I_0}{I}\right)_{\nu_{\max}}\Big/\log_e\left(\frac{T_0}{T}\right)_{\nu_{\max}}$													
2.0	1.00	1.00	1.01	1.02	1.03	1.04	1.06	1.09	1.13	1.18	1.24	1.32	1.44	1.61
1.8	1.00	1.01	1.01	1.02	1.03	1.04	1.06	1.09	1.13	1.18	1.24	1.32	1.44	1.59
1.6	1.00	1.01	1.01	1.02	1.03	1.04	1.06	1.09	1.13	1.18	1.24	1.32	1.43	1.58
1.4	1.00	1.01	1.01	1.02	1.03	1.04	1.06	1.09	1.13	1.18	1.24	1.32	1.43	1.57
1.2	1.00	1.01	1.01	1.02	1.03	1.04	1.06	1.09	1.13	1.17	1.24	1.31	1.42	1.56
1.0	1.00	1.01	1.01	1.02	1.03	1.04	1.06	1.09	1.13	1.17	1.24	1.31	1.42	1.55
0.8	1.00	1.01	1.01	1.02	1.03	1.04	1.06	1.09	1.13	1.17	1.24	1.31	1.41	1.54
0.6	1.00	1.01	1.01	1.02	1.03	1.04	1.06	1.09	1.13	1.17	1.24	1.31	1.41	1.53
0.4	1.00	1.01	1.01	1.02	1.03	1.04	1.06	1.09	1.13	1.17	1.23	1.30	1.40	1.53
0.2	1.00	1.01	1.01	1.02	1.03	1.04	1.06	1.09	1.13	1.17	1.23	1.30	1.40	1.52
$s/\Delta\nu^a_{1/2}$	0.00	0.05	0.10	0.15	0.20	0.25	0.30	0.35	0.40	0.45	0.50	0.55	0.60	0.65

TABLE II

VALUES OF $\Delta\nu^a_{1/2}/\Delta\nu^t_{1/2}$ IN TERMS OF THE APPARENT PEAK INTENSITY, $\log_e(T_0/T)_{\nu_{\max}}$ AND OF THE RATIO OF THE SLIT WIDTH TO THE APPARENT HALF-INTENSITY BAND WIDTH, $s/\Delta\nu^a_{1/2}$

$\log_e(T_0/T)_{\nu_{\max}}$	$\Delta\nu^a_{1/2}/\Delta\nu^t_{1/2}$													
2.0	1.00	1.00	1.01	1.02	1.03	1.04	1.06	1.09	1.13	1.17	1.22	1.28	1.36	1.51
1.8	1.00	1.00	1.01	1.02	1.03	1.05	1.07	1.10	1.14	1.18	1.23	1.29	1.38	1.53
1.6	1.00	1.00	1.01	1.02	1.03	1.05	1.07	1.10	1.14	1.18	1.24	1.31	1.40	1.55
1.4	1.00	1.00	1.01	1.02	1.03	1.05	1.08	1.11	1.15	1.19	1.25	1.33	1.43	1.58
1.2	1.00	1.00	1.01	1.02	1.03	1.05	1.08	1.11	1.15	1.20	1.27	1.35	1.45	1.60
1.0	1.00	1.00	1.01	1.02	1.03	1.05	1.08	1.12	1.16	1.21	1.28	1.37	1.48	1.63
0.8	1.00	1.00	1.01	1.02	1.03	1.06	1.09	1.12	1.16	1.22	1.30	1.39	1.51	1.66
0.6	1.00	1.00	1.01	1.02	1.04	1.06	1.09	1.13	1.17	1.23	1.31	1.41	1.54	1.70
0.4	1.00	1.00	1.01	1.02	1.04	1.06	1.09	1.13	1.18	1.24	1.32	1.43	1.57	1.75
0.2	1.00	1.00	1.01	1.02	1.04	1.07	1.10	1.14	1.19	1.25	1.34	1.46	1.60	1.80
$s/\Delta\nu^a_{1/2}$	0.00	0.05	0.10	0.15	0.20	0.25	0.30	0.35	0.40	0.45	0.50	0.55	0.60	0.65

mately the condition for the slit width s being equal to the true half-band width $\Delta^t_{1/2}$. It is seen that the quantities $\frac{\log_e(I_0/I)_{\nu_{\max}}}{\log_e(T_0/T)_{\nu_{\max}}}$ and $\Delta\nu^a_{1/2}/\Delta\nu^t_{1/2}$ depend mainly on the ratio of the slit width to the half-band width and to a much lesser extent on the peak intensity of the band, the variation being greater for larger values of $s/\Delta\nu^a_{1/2}$.

Comparison of Some Experimental Band Shapes with Lorentz Curves Modified by the Use of Finite Resolving Power.—In order to compare the shapes of infrared absorption bands in liquids with Lorentz curves modified by the use of finite resolving power, it is necessary to select absorption bands which are known to be single and free from overlapping by neighboring bands. The latter condition is not easily satisfied since absorption bands in liquids produce measurable absorptions even at 100 cm.$^{-1}$ from the band center. The three bands shown in Fig. 1 have been selected for comparison purposes in addition to the carbonyl stretching bands of the three ketosteroids taken from the work discussed in the following paper.[10]

The band shapes were determined under similar conditions to those described in the following paper.[10] A sodium chloride prism was used for the dichloroethylene, methyl alcohol and benzene bands, the frequencies being calibrated against the data of Oetjen, Kao and Randall[34] for ammonia. The ketosteroid spectra were calibrated against the water vapor data of Nielsen.[35] The estimated accuracy of the band intensities is ±0.5% absorption for the rock salt spectra and ± 1.0% for the ketosteroid spectra, the latter being measured in a region of atmospheric absorption. The relative band frequencies are probably accurate to ± 0.2 cm.$^{-1}$.

Slit widths were calculated from equation 8 using the refractive index data of Schaefer and Matossi.[36] The apparent peak intensities and half-intensity widths of the bands were measured and the true values of these quantities deduced from Tables I and II. Apparent band shapes were computed from equation 7 and compared with the band shapes determined experimentally (see Fig. 4).

In general the agreement between the computed and observed curves lies within the limits of experimental error, particularly in the central regions of the bands. Small deviations may occur in the "wings" of the absorption bands, but in these regions the computed curves are sensitive to the values taken for the half-intensity band widths. In the case of the methyl alcohol and benzene bands, the agreement between the computed and observed curves on the low frequency side of the former and

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[34] R. A. Oetjen, C. L. Kao and H. M. Randall, *Rev. Sci. Instruments*, **13**, 515 (1942).

[35] H. H. Nielsen, *Phys. Rev.*, **59**, 565 (1941).

[36] C. Schaefer and F. Matossi, "Das Ultrarote Spektrum," Springer Verlag, Berlin, 1930, p. 46.

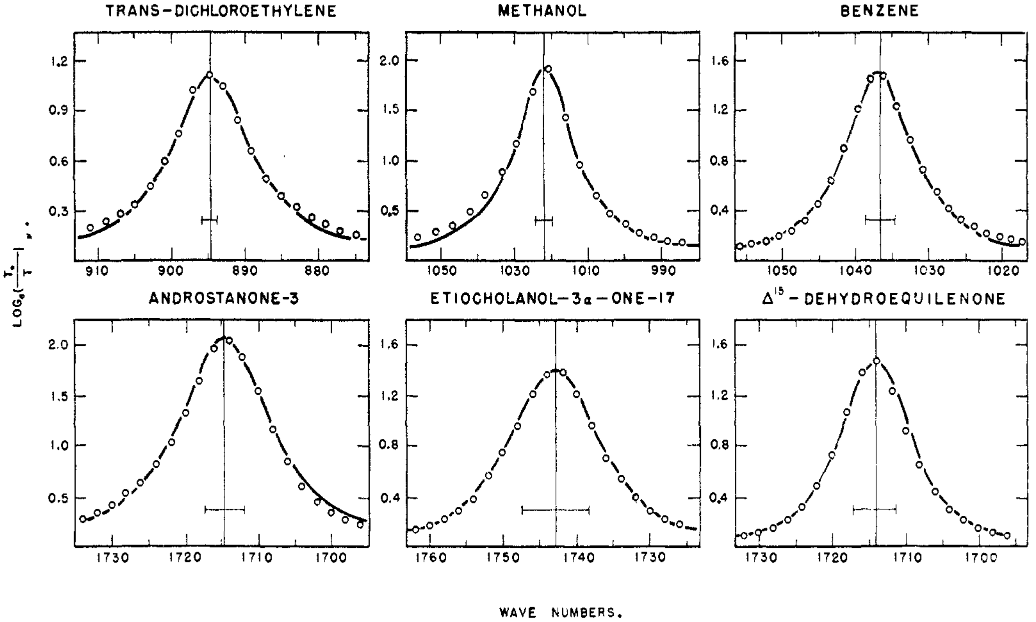

Fig. 4.—Comparison of some experimental band shapes with Lorentz curves modified by the use of finite resolving power: O, experimental points; —— "apparent" Lorentz curve.

on the high frequency side of the latter is particularly good. On the other sides of these bands, however, deviations are found. These may be correlated with the presence of weak neighboring absorption bands (see Fig. 1).

The shapes of several other single absorption bands have been compared with Lorentz curves modified by the use of finite resolving power and similar agreement found. Hence the experimental evidence suggests that the *true* shapes of many *single* absorption bands in the liquid phase approximate closely to Lorentz curves.

Methods for the Determination of True Integrated Absorption Intensities

Two methods for the determination of true integrated absorption intensities from experimental absorption curves have been described by Bourgin[20] and by Wilson and Wells[11] and have been applied to gases. These methods involve extrapolations of measurements of band areas made at a series of different concentrations or path lengths to zero concentration or path length and are equally applicable in the case of liquids and solutions. A serious limitation lies in the fact that these extrapolations are very sensitive to measurements at small concentrations or path lengths when the experimental errors in determining band areas are large. To obtain satisfactory extrapolations it is necessary to make measurements at a considerable number of concentrations or path lengths. If the true shape of the absorption band is known, it is possible to calculate the nature of these extrapolation curves for various slit functions, and hence obtain true integrated absorption coefficients from measurements at a single concentration or path length (see methods II and III).

A more direct method for obtaining true integrated absorption intensities involves integration of the equation for the true shape of the absorption band and will be considered first.

Method I. The Method of Direct Integration. —If the true shape of an infrared absorption band in the liquid phase is given by equation 6, then by combining equations 2 and 6 we get

$$A = \frac{1}{cl}\int_{-\infty}^{+\infty} \frac{a}{(\nu - \nu)^2 + b^2}\, d\nu = \frac{1}{cl} \times \frac{a}{b} \tan^{-1}\left[\frac{\nu - \nu_0}{b}\right]_{-\infty}^{+\infty} = \frac{1}{cl} \times \frac{\pi a}{b} \qquad (9)$$

The peak intensity of the band is given by

$$\log_e \left(\frac{I_0}{I}\right)_{\nu_{\max}} = \frac{a}{b^2} \qquad (10)$$

and the half-intensity width, $\Delta\nu^t_{1/2}$, by

$$\Delta\nu^t_{1/2} = 2b \qquad (11)$$

Hence equation (9) may be rewritten

$$A = \frac{\pi}{2} \times \frac{1}{cl} \log_e \left(\frac{I_0}{I}\right)_{\nu_{\max}} \times \Delta\nu^t_{1/2} \qquad (12)$$

Since the band shape obtained experimentally is an apparent band shape, it is convenient to rewrite equation (12) in the form

$$A = \frac{K}{cl} \log_e \left(\frac{T_0}{T}\right)_{\nu_{\max}} \times \Delta\nu^a_{1/2} \qquad (13)$$

where

$$K = \frac{\pi}{2} \times \frac{\log_e(I_0/I)_{\nu_{\max}}}{\log_e(T_0/T)_{\nu_{\max}}} \times \frac{\Delta\nu^t_{1/2}}{\Delta\nu^a_{1/2}} \qquad (14)$$

The true and apparent values of the peak intensities and half intensity widths are related to one another and to the half intensity widths (see Tables I and II), hence it is possible to construct a similar Table for K (see Table III). It is seen that K differs from $\pi/2$ by more than 5% only for values of $s/\Delta\nu^a_{1/2}$ greater than 0.40, and then only in the case of very strong or very weak bands. For apparent peak intensities of ~1.4 (~75% absorption) the

TABLE III

VALUES OF K IN TERMS OF THE APPARENT PEAK INTENSITY, $\log_e(T_0/T)\nu_{max}$ AND OF THE RATIO OF THE SLIT WIDTH TO THE APPARENT HALF-INTENSITY BAND WIDTH, $s/\Delta\nu^a_{1/2}$

$\log_e \left(\frac{T_0}{T}\right)_{\nu_{max}}$	K													
2.0	1.57	1.57	1.57	1.57	1.57	1.57	1.57	1.57	1.58	1.59	1.60	1.62	1.65	1.68
1.8	1.57	1.57	1.57	1.57	1.57	1.57	1.57	1.57	1.57	1.58	1.58	1.60	1.62	1.64
1.6	1.57	1.57	1.57	1.57	1.57	1.57	1.57	1.57	1.57	1.57	1.57	1.58	1.59	1.60
1.4	1.57	1.57	1.57	1.57	1.57	1.56	1.56	1.56	1.56	1.56	1.56	1.56	1.56	1.56
1.2	1.57	1.57	1.57	1.57	1.56	1.56	1.56	1.55	1.55	1.54	1.54	1.54	1.54	1.53
1.0	1.57	1.57	1.57	1.56	1.56	1.55	1.55	1.54	1.54	1.53	1.52	1.52	1.51	1.50
0.8	1.57	1.57	1.57	1.56	1.56	1.55	1.54	1.53	1.52	1.51	1.50	1.49	1.48	1.47
0.6	1.57	1.57	1.56	1.56	1.55	1.55	1.54	1.53	1.51	1.50	1.48	1.46	1.45	1.43
0.4	1.57	1.57	1.56	1.56	1.55	1.54	1.53	1.52	1.50	1.48	1.46	1.44	1.41	1.38
0.2	1.57	1.57	1.56	1.56	1.55	1.54	1.53	1.51	1.49	1.47	1.44	1.41	1.37	1.33
$s/\Delta\nu^a_{1/2}$.	0.00	0.05	0.10	0.15	0.20	0.25	0.30	0.35	0.40	0.45	0.50	0.55	0.60	0.65

departure of K from $\pi/2$ is only $\sim 1\%$ for all values of $s/\Delta\nu^a_{1/2}$ up to 0.65.[37]

Method II. Extension of the Method of Wilson and Wells.—In this method[11] the true integrated absorption intensity of a band is obtained by extrapolating the apparent integrated absorption intensity at a series of different concentrations or path lengths to zero concentration or path length. The method assumes (i) the incident intensity is constant over the slit width and (ii) the resolving power is constant over the width of the band. The nature of the extrapolation is dependent on the band shape and the resolving power used. Assuming the true shape of the absorption band to be given by equation 6 the shape of the extrapolation curve for various ratios of the slit width to half-intensity band width was determined as follows.

A series of apparent band shapes was calculated by means of equation 7 for a fixed value of $s/\Delta\nu^t_{1/2}$ and various values of the true peak intensity. The calculations were extended on either side of the band center so that corrections to be applied for the area under the "wings" of the absorption band were less than 10% (see following section). The areas under the apparent absorption curves were measured and corrections for the areas under the wings applied. The ratios of the apparent to the true band areas, *viz.*

$$\frac{\int \log_e(T_0/T)_\nu \, d\nu}{\int \log_e(I_0/I)_\nu \, d\nu}$$

were plotted against the apparent peak intensities $\log_e (T_0/T)\nu_{max}$ (Fig. 5) and found to lie very close to a straight line with a slight negative slope θ. Values of θ for various values of $s/\Delta\nu^t_{1/2}$ between 0.1 and 1.0 were determined and are given in Table IV.

TABLE IV

VALUES OF θ IN TERMS OF THE RATIO OF THE SLIT WIDTH TO THE TRUE HALF INTENSITY BAND WIDTH, $s/\Delta\nu^t_{1/2}$

$s/\Delta\nu^t_{1/2}$	θ
0.1	−0.002
.2	− .004
.3	− .008
.4	− .013
.5	− .020
.6	− .028
.7	− .036
.8	− .046
.9	− .057
1.0	− .070

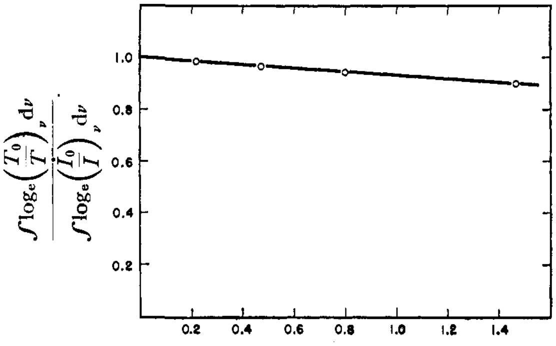

Fig. 5.—Graph of $\frac{\int \log_e(T_0/T)_\nu d\nu}{\int \log_e(I_0/I)_\nu d\nu}$ against the apparent peak intensity $\log_e(T_0/T)_{\nu max.}$ for a series of Lorentz curves scanned with a slit width s equal to the true half intensity band width $\Delta\nu_{1/2}{}^t$.

The true integrated intensity of a band whose shape is given by equation 6 is obtained by plotting the apparent integrated absorption intensity measured at several different concentrations or path lengths against the apparent peak intensity $\log_e(T_0/T)\nu_{max}$ and determining the best straight line with intercept A and slope $A\theta$ (see Fig. 2 of following paper). The value of A derived in this way is considerably more accurate than the value obtained by using the method of least squares to determine the best straight line since the latter method is dependent on measurements of weak bands where experimental errors are large.

Alternatively the true integrated intensity (A) may be obtained from a single measurement of the apparent integrated absorption intensity ( ) by means of the relation

$$B = A + A\theta \log_e(T_0/T)\nu_{max} \qquad (15)$$

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[37] J. J. Fox and A. E. Martin (*Proc. Roy. Soc.* (*London*), **A167**, 257 (1938)) considered various reasonable shapes for infrared absorption bands of liquids and concluded theoretically that K should lie between 1 and $\pi/2$. Using a grating spectrometer with a narrow slit they found experimentally that for many bands $K = 1.4$. It is doubtful however whether they considered the "wing" correction (see later) in determining their measured band areas. Morever, they did not note any slight dependence of K on the peak intensity of the band for a given slit width.

or

$$A = \frac{B}{1 + \theta \log_e(T_0/T)_{\nu_{\max}}} \quad (16)$$

where it should be noted that θ is negative (*i.e.*, $A > B$).

Since the values of θ are small the corrections to be applied to the apparent integrated absorption intensities (B) are also small and are linearly dependent on $\log_e(T_0/T)_{\nu_{\max}}$. Using a slit width equal to one-half the true half-intensity band width ($s/\Delta\nu^t_{1/2} = 0.5$) and an apparent peak intensity of 1.4 (~75% absorption), the correction to be applied is ~3% and is of the same order as the accuracy of the measurement of B. A more important factor to be considered is the correction for the area under the "wings" of the absorption band.

"Wing" Correction.—In practice the band area is measured only for a finite frequency range (~50 cm.$^{-1}$) on both sides of the band center, since the absorption falls to the same order as the experimental error in the absorption measurement. If the band is considered to extend indefinitely, however, the residual area under the "wings" may be an appreciable fraction of the total area of the band, for although the absorption is small the frequency interval by which it is multiplied is very large.

If the true band shape is given by equation 6 and the area measured over a frequency interval ($\nu - \nu_0$) on either side of the band center, the ratio of the measured area to the total area of the band may be shown from equation 9 to be

$$\text{measured area/total area} = \tan^{-1}\frac{\nu - \nu_0}{b} \Big/ \pi/2 \quad (17)$$

The correction to be applied for the area under the wings of the absorption band may be expressed most conveniently as a percentage of the measured band area as follows

$$\%\ \text{correction} = \frac{\pi/2 \tan^{-1}\dfrac{\nu - \nu_0}{b}}{\tan^{-1}\dfrac{\nu - \nu_0}{b}} \times 100 \quad (18)$$

Values of this correction for various values of $(\nu - \nu_0)/b$ are given in Table V. For a band with a true half-intensity width of 10 cm.$^{-1}$ and a true peak intensity of 1.4 (~75% absorption), the intensity falls to 1% absorption at ~60 cm.$^{-1}$ from the band center. If the band area is measured over this frequency interval, the correction to be applied for the residual area under the wings of the band is seen from Table V to be ~6%. In the measurements described in the following paper it was found convenient to measure band areas to 40 cm.$^{-1}$ from the band center in which case the correction was ~10%.

TABLE V

"WING" CORRECTIONS FOR INTEGRATED ABSORPTION AREAS (METHOD II)

$\frac{\nu - \nu_0}{b}$	% Cor.	$\frac{\nu - \nu_0}{b}$	% Cor.	$\frac{\nu - \nu_0}{b}$	% Cor.
4.0	18.5	7.0	9.9	10.0	6.8
4.2	17.5	7.2	9.6	10.5	6.4
4.4	16.6	7.4	9.4	11.0	6.1
4.6	15.8	7.6	9.1	11.5	5.8
4.8	15.1	7.8	8.8	12.0	5.6
5.0	14.4	8.0	8.6	12.5	5.3
5.2	13.8	8.2	8.4	13.0	5.1
5.4	13.2	8.4	8.1	13.5	4.9
5.6	12.7	8.6	7.9	14.0	4.7
5.8	12.2	8.8	7.8	14.5	4.6
6.0	11.8	9.0	7.6	15.0	4.4
6.2	11.3	9.2	7.4		
6.4	10.9	9.4	7.2		
6.6	10.6	9.6	7.0		
6.8	10.3	9.8	6.9		

The wing corrections above have been calculated for a "true" band whose shape is given by equation 6. For an "apparent" band the wing corrections are more difficult to compute, but may be estimated as follows.

In the case where $s = \Delta\nu^t_{1/2}$, it is found that for $(\nu - \nu_0)/b \geqslant 10$, the difference between the true and apparent intensity at any frequency ν is less than 1%. The area under the wings of the apparent absorption band may therefore be taken as equal to the area under the wings of the true absorption band to within 1%. If this area is added to the area under the apparent absorption curve between the limits calculated, the total area under the apparent absorption curve is obtained. The area under the wings of the apparent absorption band for any other value of $(\nu - \nu_0)/b$ may now be obtained by subtracting the area of the band between these limits from the total area under the band.

If the wing corrections are expressed as percentages of the measured band area (*cf.* equation 18) it is found that provided $(\nu - \nu_0)/b \geqslant 10$ the wing corrections are the same as for the true band to within 1% of the measured band, while if $10 \geqslant (\nu - \nu_0)/b \geqslant 5$, the corrections agree to within 2%. Hence, provided these conditions are satisfied, the wing corrections given in Table V are sufficiently accurate for experimental purposes.

Method III. Extension of the Method of Absorption Areas.—This method was used first by Bourgin[20] and later discussed by Wilson and Wells.[11] The area, A', under an absorption curve expressed as fractional absorption, $1 - (I/I_0)_\nu$, *versus* frequency ν, is given by

$$A' = \int \left\{1 - \left(\frac{I}{I_0}\right)_\nu\right\} d\nu \quad (19)$$

Substituting equation 1 and expanding we get

$$\frac{A'}{cl} = \int \left\{\alpha_\nu - \frac{\alpha_\nu^2}{2!}cl + \frac{\alpha_\nu^3}{3!}(cl)^2 - \ldots\right\} d\nu \quad (20)$$

and

$$\lim_{cl \to 0} \frac{A'}{cl} = \int \alpha_\nu d\nu = A \quad (21)$$

The true integrated absorption intensity of a band may therefore be obtained by plotting A'/cl against cl and extrapolating $cl \to 0$. Since the area under an absorption curve is independent of the resolving power used,[38,39] the nature of the extrapolation is also independent of the resolving power and is dependent only on the band shape. If the shape of the true absorption curve is given by equation 6, then by substituting into equation 20 it can be shown in a few stages that

$$\frac{A'}{cl} = A\left\{1 - \frac{1}{2!} \times \frac{1}{2}\log_e\left(\frac{I_0}{I}\right)_{\nu_{\max}} + \frac{1}{3!} \times \frac{3.1}{4.2}\left[\log_e\left(\frac{I_0}{I}\right)_{\nu_{\max}}\right]^2 - \frac{1}{4!} \times \frac{5.3.1.}{6.4.2.}\left[\log_e\left(\frac{I_0}{I}\right)_{\nu_{\max}}\right]^3 + \ldots\right\} \quad (22)$$

Hence A may be obtained by plotting A'/cl against $\log_e(I_0/I)_{\nu_{\max}}$ and extrapolating to $\log_e(I_0/$

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(38) D. M. Dennison, *Phys. Rev.*, **31**, 503 (1928).

(39) J. R. Nielsen, V. Thornton and E. B. Dale, *Rev. Modern Phys.*, **16**, 307 (1944).

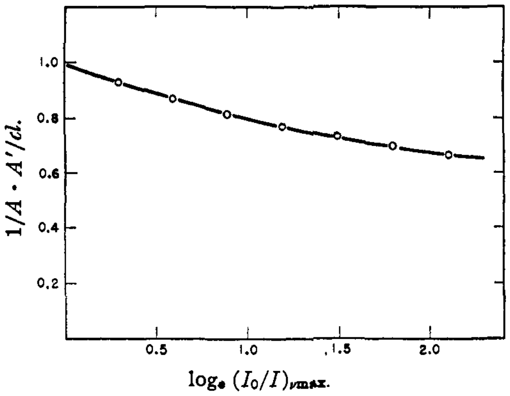

Fig. 6.—Graphical extrapolation for the method of absorption areas assuming a Lorentz curve for the true band shape and a triangular slit function.

$I)\nu_{\max} = 0$. The nature of this extrapolation may be determined by evaluating equation 22 for various values of $\log_e(I_0/I)\nu_{\max}$. If $1/A \times A'/cl$ is plotted against $\log_e(I_0/I)\nu_{\max}$, the extrapolation is found to be a shallow curve (Fig. 6). If, however, the reciprocal $A \times cl/A'$ is plotted against $\log_e(I_0/I)\nu_{\max}$, the extrapolation is found to approximate very closely to a straight line with slope 0.25 (Fig. 7). Appreciable deviations from linearity occur only for values of $\log_e(I_0/I)\nu_{\max} > 1.5$, *i.e.*, for true peak intensities exceeding 80%.

The most convenient way to obtain A is to rewrite equation 22 in the form

$$A = \varphi \times A'/cl \tag{23}$$

where

$$\varphi = 1 \Big/ \left\{ 1 - \frac{1}{2!} \times \frac{1}{2} \log_e(I_0/I)\nu_{\max} + \frac{1}{3!} \times \frac{3.1}{4.2} [\log_e(I_0/I)\nu_{\max}]^2 - \ldots \right\} \tag{24}$$

Values of φ for different values of $\log_e(I_0/I)\nu_{\max}$ are given in Table VI.

TABLE VI

VALUES OF φ FOR VARIOUS VALUES OF LOG$_e$ $(I_0/I)\nu_{\max}$

$\log_e (I_0/I)\nu_{\max}$	φ	$\log_e (I_0/I)\nu_{\max}$	φ
0.0	1.000	1.0	1.248
.1	1.025	1.1	1.272
.2	1.050	1.2	1.296
.3	1.075	1.3	1.320
.4	1.100	1.4	1.344
.5	1.125	1.5	1.368
.6	1.149	1.6	1.391
.7	1.174	1.7	1.415
.8	1.199	1.8	1.438
.9	1.223	1.9	1.462
1.0	1.248	2.0	1.484

"Wing" Correction.—As in method II, it is possible to to measure the area under the absorption band only between finite limits on either side of the band center, and it is necessary to apply a correction for the area under the wings of the absorption band to obtain A'. If the absorption area is measured over a frequency range $\nu - \nu_0$ on either side of the band center, the area w under the wings is

$$w = 2\int_{\nu - \nu_0}^{\infty} \left(1 - e^{\frac{-a}{(\nu - \nu_0)^2 + b^2}}\right) d\nu \tag{25}$$

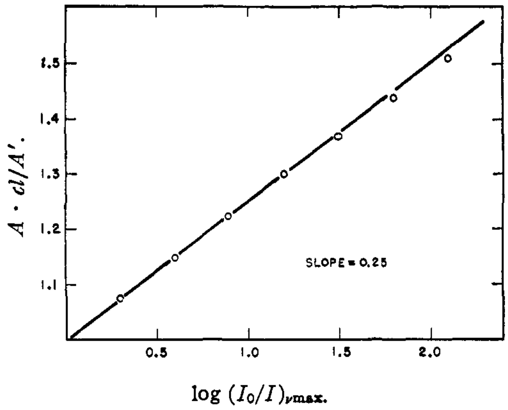

Fig. 7.—Linear extrapolation for the method of absorption areas obtained by plotting $(A \times cl)/A'$ against $\log_e (I_0/I)_{\nu\max}$

It has been shown by Bourgin[39] that provided $(\nu - \nu_0)/b > 20$ this integral may be approximated to

$$w = \frac{\Delta\nu^t_{1/2} \log_e (I_0/I)\nu_{\max}}{\frac{\nu - \nu_0}{b}} \tag{26}$$

with an accuracy of 1%. A table of wing corrections was therefore constructed as follows.

A series of absorption bands having the same half-intensity width but different peak intensities were plotted over a frequency interval $\nu - \nu_0$, on either side of the band center extending to $20b$. The areas under these bands were measured, and wing corrections calculated from equation 26. The total areas of the bands were thus found. The wing corrections for various values of $(\nu - \nu_0)/b$ were then determined by subtracting the areas of the band within these limits from the total area of the band.

The wing corrections were expressed as percentages of the measured band area (*cf.* equation 18) and are given in Table VII.[40] Although these corrections are applicable strictly only to bands whose shape is given by equation 6, the error introduced by using these corrections for "apparent" absorption curves will in general not exceed 2% of the measured band area and is sufficiently small for experimental purposes.

Comparison of the Methods.—All three methods depend to a greater or lesser extent on the assumptions of a Lorentz curve for the true band shape and on a triangular slit function. These assumptions are most fundamental to Method I, which has the principal advantage of being extremely rapid. It depends on measurements at three points on the band only whereas the other methods involve measurements over the whole of the experimental curve. Nevertheless, the data in the following paper show that the results obtained by method I agree with those obtained by methods II and III to within 5–10%.

Method II depends on the band shape and the slit function to the extent of the wing correction and the slope of the extrapolation, both of which are fairly small quantities. In method III the wing correction depends mainly on the band shape and only to a very slight extent on the slit function, whereas the extrapolation depends entirely on the band shape and is independent of the slit function. The data in the following paper show that the results obtained by methods II and III always agree to within 2%. This might be expected since, in so

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(40) It may be noted that the wing corrections in method III as $\log_e \left(\frac{I_0}{I}\right) \nu_{\max} \rightarrow 0$ are the same as in method II. This follows from equation 20.

TABLE VII

"WING" CORRECTIONS FOR ABSORPTION AREAS (METHOD III)

$\text{og}_e(I_0/I)\nu_{\max}$	4	5	6	7	8	9	10	11	12	13	14	15
2.0	29.9	22.9	18.6	15.6	13.4	11.8	10.6	9.4	8.6	7.9	7.3	6.8
1.8	28.7	22.0	17.9	15.0	13.0	11.4	10.2	9.1	8.3	7.6	7.0	6.5
1.6	27.5	21.1	17.2	14.4	12.5	11.0	9.8	8.8	8.0	7.4	6.8	6.3
1.4	26.3	20.2	16.5	13.8	12.0	10.6	9.4	8.5	7.7	7.1	6.6	6.1
1.2	25.0	19.3	15.7	13.2	11.5	10.1	9.0	8.1	7.4	6.8	6.3	5.8
1.0	23.8	18.4	15.0	12.6	11.0	9.7	8.6	7.8	7.1	6.5	6.0	5.6
0.8	22.6	17.5	14.3	12.0	10.5	9.3	8.3	7.5	6.8	6.3	5.8	5.4
0.6	21.4	16.6	13.6	11.5	10.0	8.8	7.9	7.2	6.5	6.0	5.5	5.2
0.4	20.3	15.8	12.9	10.9	9.5	8.4	7.5	6.8	6.2	5.7	5.3	5.0
0.2	19.3	15.0	12.3	10.5	9.1	8.1	7.2	6.5	5.9	5.4	5.0	4.7

$(\nu - \nu_0)/b$.

far as the initial assumptions are valid, the two methods are mathematically equivalent.

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The Intensities of Carbonyl Bands in the Infrared Spectra of Steroids[1]

BY R. NORMAN JONES, D. A. RAMSAY, D. S. KEIR AND KONRAD DOBRINER

The application of the methods which are described in the previous paper to the determination of the intensities of C=O stretching bands in steroids is illustrated. Correlations between band intensities and molecular structures have been established on the basis of measurements on 55 steroids. The integrated absorption intensities of different types of carbonyl groups vary by a factor of four but the intensity for a given type of carbonyl group is sensibly constant in different compounds. The ketone intensity does not vary appreciably with the position of the carbonyl group in the steroid nucleus, but is significantly different when the carbonyl group is in a side chain. Systematic changes in intensity are observed when the carbonyl group is conjugated or when a halogen atom is introduced at a vicinal methylene group. In the di- and polycarbonyl compounds investigated the carbonyl intensities were found to be additive within the limits of experimental error. Such measurements permit the number of carbonyl groups in a compound to be determined even where the bands overlap completely, and have been applied to the elucidation of the structure of steroids isolated from natural sources. Integrated absorption intensities are found to give more satisfactory structural correlations than maximal molecular extinction coefficients.

Introduction

The infrared absorption band associated with the stretching vibration of the carbonyl group normally occurs between 1650 and 1800 cm.$^{-1}$. In solution the exact position of the band maximum is influenced by the solvent and by the molecular structure in the immediate environment of the carbonyl group. Characteristic band positions have been established for different types of carbonyl functions in steroid[2] and from observation of the number and position of the carbonyl bands it is often possible to determine both the number and the location of the carbonyl groups present in a steroid molecule.[2,3]

Ambiguity can arise in the interpretation of such bands, as certain different carbonyl groups absorb near the same frequency. For example, the acetates of 3-, 6-, 7-, 11-, 12-, 17- and 20-steroid alcohols absorb between 1735 and 1745 cm.$^{-1}$ in carbon disulfide solution, and from the band position alone it is possible neither to distinguish among these structures nor to determine how many acetate groups are present in the molecule. The carbonyl bands of the 17-ketone and the δ-lactone groups also absorb in the same range and may be obscured in the spectra of acetylated derivatives.

The characterization of certain types of di- and polyketosteroids from the infrared spectrum is also rendered impossible because of the superposition or extensive overlap of the bands. Ketosteroids containing carbonyl groups at position 3-, 6-, 7-, 11-, 12- and 20- all absorb between 1706 and 1720 cm.$^{-1}$ in carbon disulfide solution, and, although two maxima have been resolved in the spectrum of one 3,20-diketosteroid,[3] the other diketosteroids involving these positions give one band only.

A distinction between carbonyl systems giving overlapping bands might be achieved from an analysis of the band intensities, and a general study

[1] Published as Contribution No. 2566 from the Laboratories of the National Research Council of Canada, and No. XI in the series "Studies in Steroid Metabolism," Presented, in part, at a Symposium on Molecular Spectroscopy held at the Ohio State University, June, 1948, and at the Pittsburgh Conference on Analytical and Applied Spectroscopy, March, 1951. In this paper frequent references are made to the tables in the preceding paper, and this is indicated by an asterisk, *viz.*, for Table I* see page 75 and for Table I see page 83.

[2] R. N. Jones, P. Humphries and K. Dobriner, THIS JOURNAL, **72**, 956 (1950), and earlier publications.

[3] R. N. Jones and K. Dobriner, *Vitamins and Hormones*, **7**, 293 (1949).