On the Determination of Absolute Intensities from Single- and Multiple-Path Absorption Measurements

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The physical principles involved in conventional absolute intensity measurements are reviewed. Experimental difficulties rule out the use of extrapolation techniques for some spectral transitions. For this reason it is of interest to re-examine the possibility of using total absorption measurements, in conjunction with the curves of growth, for making intensity estimates. Extrapolation methods yield results which are independent of spectral line shape. Use of the curves of growth, on the other hand, implies the assumption that the line contour can be described by combined Doppler and Lorentz broadening.

The curves of growth permit a unique correlation between total absorption and f-value either for spectral lines with pure Doppler broadening or for pure collision broadening. Furthermore, a simple experimental procedure can be devised for estimating both the absolute intensity and the spectral line profile on the basis of single-path and multiple-path absorption measurements. The suggested procedure involves absorption measurements for optical densities (path lengths) under conditions in which the integrated fractional absorption is independent of spectral line shape.

For absolute intensity estimates on isolated spectral lines in ultraviolet spectra probably the most widely used procedure involves measurement of the integrated fractional absorption, followed by attempts at estimation of f-values through the use of the curves of growth. If accurate measurements can be made for sufficiently small optical densities, unambiguous interpretation of the results is possible since the fractional absorption is independent of spectral line shape. Less satisfactory is the type of interpretation used, for example, in the determination of absolute f-values for lines belonging to $^{2}S$→$^{2}II$ transitions of OH. In this case the integrated fractional absorption depends upon both line shape and absolute intensity. Consequently, fitting of observed data to theoretical curves for relative intensities involves such doubtful assumptions as uniform line shape for all of the measured lines, relative intensity estimates which neglect vibration-rotation interactions, etc. It is evident that a more satisfactory approach for conditions corresponding to nonlinear portions of the curves of growth must involve two independent measurements for each spectral line in order to determine the two unknowns involved, viz., line shape and f-value. This suggested procedure is applicable to all spectral lines which are adequately described by combined Doppler and Lorentz broadening, irrespective of the spectral region in which the lines under study occur.

Reliable infrared intensity measurements for entire vibration-rotation bands can be carried out by judicious use of extrapolation techniques combined with suitable methods for pressure broadening. Since the experimental conditions required for intensity estimates are sometimes difficult to meet, particularly for diatomic molecules, use of the procedure based on the curves of growth is indicated in some cases.

There are two basic assumptions involved in the use of the curves of growth for line shape and intensity estimates. These are: (1) the spectral lines under study have a contour which is described adequately by a representation based on Lorentz and Doppler broadening; (2) the measured integrated fractional absorption is substantially independent of experimental slit width. There is experimental evidence that the first assumption is often a useful empirical rule in the sense that observed experimental data can be made to fit a simplified spectral line contour, although the actual line shape may not correspond exactly to the Doppler-Lorentz broadening formula. It is easily shown that

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8 For discussions of spectral line shape see, for example, H. Margenau and W. W. Watson, Revs. Modern Phys. 8, 22 (1936); J. H. Van Vleck and V. F. Weisskopf, ibid. 17, 227 (1945); P. W. Anderson, Phys. Rev. 76, 647 (1949).
the second statement is correct, in principle; errors resulting from lack of experimental sensitivity will be discussed in a subsequent publication.

In Sec. II we present a brief review of the physical principles involved in the use of extrapolation techniques for absolute intensity measurements. Absolute intensity and line-shape estimates through the curves of growth are considered in Sec. III. Application of the proposed procedure to $^2S\rightarrow^2\Pi$ transitions of OH, (0,0)-band, is described in Sec. IV. Representative calculations for spectral lines belonging to the fundamental vibration-rotation band of CO are given in Sec. V.

II. EXTRAPOLATION TECHNIQUES FOR ABSOLUTE INTENSITY MEASUREMENTS

The fractional absorption, $A(\omega)$, and the fractional transmission, $T(\omega)$, are related through the expression

$$ A(\omega) = 1 - T(\omega). $$

If $P(\omega)$ is the spectral absorption coefficient at the wave number $\omega$ and $X$ equals the optical density, then

$$ \int_{\omega_1}^{\omega_2} A(\omega) d\omega = \int_{\omega_1}^{\omega_2} \left[ 1 - \exp[-P(\omega)X] \right] d\omega $$

independently of the experimental slit function, provided the integration interval from $\omega_1$ to $\omega_2$ exceeds the wave-number range, for which $P(\omega)$ vanishes, by the experimental slit width $\Delta\omega^*$. It should be noted also that the validity of Eq. (2) does not depend on the functional form of $P(\omega)$ provided $P(\omega)$ vanishes for $\omega = \omega_1 + \Delta\omega^*$ and for $\omega = -\Delta\omega^* \leq \omega$. From Eq. (2) is apparent that

$$ S_K = \int_{\omega_1}^{\omega_2} P(\omega) d\omega = \lim_{X \to \infty} \left[ \frac{1}{X} \right] \int_{\omega_1}^{\omega_2} A(\omega) d\omega $$

where $S_K$ represents the integrated intensity of the spectral line under study whose center is assumed to lie at the wave number $\omega_K$. The validity of Eq. (3) for all slit functions and line shapes forms the basis of extrapolation methods for the determination of absolute intensities. Extrapolation methods will fail to yield reliable results only if $\int_{\omega_1}^{\omega_2} A(\omega) d\omega$ is not estimated correctly at very low optical densities because of lack of intrumental sensitivity. In this case the limiting curvature of a plot of $\int_{\omega_1}^{\omega_2} A(\omega) d\omega$ vs $X$ is not defined properly, and extrapolation to $X = 0$ leads to an erroneous estimate for $S_K$.

Significant absolute intensity estimates are obtained also if the experimental slit width is small compared to the line width. Under these conditions $P(\omega)$ is measured directly and

$$ S_K = \int_{\omega_1}^{\omega_2} P(\omega) d\omega = -\frac{1}{X} \int_{\omega_1}^{\omega_2} [\ln T(\omega)] d\omega $$

defines the integrated intensity. Experimental conditions justifying the use of Eq. (4) can be approached at elevated pressures. In practice a combination of pressure broadening and extrapolation to zero optical pathlength leads to the most desirable results.

It is apparent from the preceding considerations that there is a need for methods of obtaining reliable intensity estimates under conditions where pressure broadening and/or extrapolation to zero optical pathlength is not feasible. For this reason we propose to re-examine the use of the curves of growth for the interpretation of integrated fractional absorption measurements, particularly under conditions in which the measured results are a sensitive function of the line-shape parameter.

III. USE OF THE CURVES OF GROWTH FOR ABSOLUTE INTENSITY AND LINE-SHAPE MEASUREMENTS

The integrated fractional absorption is again determined through Eq. (2) while the integrated intensity $S_K$ is defined in Eq. (4). If the spectral line under study had a pure Doppler contour the (maximum) absorption coefficient at the line center would be

$$ P_K = (S_K/\omega_K) (mc^2/\pi kT)^{1/4} $$

where $m$ is the mass of the radiating molecule, $c$ equals the velocity of light, $k$ equals the Boltzmann constant, and $T$ is the absolute temperature. A spectral line with combined Doppler, collision, and natural line broadening is described conveniently by the parameter

$$ a = (b_N + b_c) (\ln 2)^{1/2} b_D, $$

where $b_N$, $b_c$, and $b_D$ denote, respectively, the natural half-width, the half-width resulting from collision (Lorentz) broadening, and the half-width produced by Doppler broadening.

The spectral absorption coefficient $P(\omega)$ entering into Eq. (2) is a linear function of $P_K'$ and depends also on the line-shape parameter $a$. In the conventional curves of growth $A(\ln 2)^{1/2} b_D$ is plotted as a function of $P_K'X$ with $a$ treated as a variable parameter, where

$$ (\ln 2)^{1/2} b_D = (1/\omega_K) (mc^2/\pi kT)^{1/4}. $$

Let $A_1$ and $A_2$ represent, respectively, the total fractional absorption for the $K$'th spectral line if the optical pathlengths have the values $X_1$ and $X_2$, respectively. It is then a simple matter to obtain $A_1$ and $A_2$ as functions of $P_K'X_1$ and $a$ for known values of $X_2/X_1$ through use of the curves of growth. Alternately, the ratio $A_2/A_1$ can be represented as a function of $P_K'X_1$.

The half-width is defined as the wave-number range for which $P(\omega)$ is greater than or equal to one-half of the spectral absorption coefficient at the line center.
and $a$, as has been done in a previous publication for the special case $X_2/X_1=2$.\textsuperscript{14}

From the measured values of $A_1$ and $A_2$ and the known ratio $X_2/X_1$ we can construct two curves relating $a$ to $P_k'X_1$. The applicable values of $a$ and $P_k'X_1$ for the absorbing system correspond to the intersection of the two curves of $a$ vs $P_k'X_1$. Finally, since $X_1$ is known from the partial pressure of absorbing gas and from the length of the gas absorption cell, $P_k'$ itself is determined. The integrated intensity $S_K$ may now be calculated from Eq. (5). Alternately, the dimensionless f-value, $f_K$, is given through the expression

$$S_K = \frac{2.379 \times 10^5 (273.1 / T) f_K(N_1 / N_T)}{X_1 \exp(-E_i / kT)}$$

where $N_1 / N_T$ represents the fraction of the total number of absorbing molecules in the lower state for the transition or transitions giving rise to the line with quantum number $K$, and $h$ is Planck’s constant.

If experimental measurements are made for a series of spectral lines belonging to a given electronic transition or vibration-rotation band, and if the relative intensities can be calculated theoretically, a simple experimental check is available for the consistency of the data as well as for the correctness of the relative intensity calculations. Thus

$$S_K = \frac{8 \pi^2 N_T}{3 h o Q} g_u(q_k) X_1 \exp(-E_i / kT) \left[1 - \exp(-h o \omega_{K}/kT)\right]$$

where $Q$ is the total partition function, $g_u$ equals the statistical weight of the upper state involved in the transition giving rise to the $K$th spectral line, $(q_k)^2$ is the square of the matrix element for the transition under study, and $E_i$ is the lower energy level of the absorbing (ground) state. From Eqs. (5) and (8) it is easily shown\textsuperscript{18} that

$$P_k' = \frac{3 h o Q}{8 \pi^2 N_T} \left(\frac{2 \pi k T}{m c^2}\right)^{1/2} \left[\exp(E_i / kT)\right]^{-1} \left[\exp(-h o \omega_{K K'}/kT)\right]^{-1} = 1.$$  \textsuperscript{(9)}

A plot of the left-hand side of Eq. (9) as a function of $K$ would be expected to show systematic deviations from unity if, for example, significant vibration-rotation interactions had been neglected in the calculation of $g_u(q_k)^2$. Alternately, if correct theoretical values are available for $g_u(q_k)^2$, then consistency of the experimental data can be verified by showing that $\ln[S_K/g_u(q_k)^2]$ is a linear function of $E_i$ with slope equal to $-1/kT$.

\textsuperscript{14} S. S. Penner, J. Chem. Phys. 21, 686 (1953).

\textsuperscript{15} The factor $\left[1 - \exp(-h o \omega_{K K'}/kT)\right]$ is practically equal to unity at all reasonable temperatures for absorption experiments in the visible and infrared regions of the spectrum.


\textsuperscript{17} G. H. Dieke and H. M. Crosswhite, Bumblebee Series Report No. 87, The Johns Hopkins University, Baltimore, November, 1948.

\textsuperscript{18} This result is based on the thermodynamic functions prepared by the National Bureau of Standards and listed in “Tables of Selected Values of Chemical Thermodynamic Properties,” Series I, Volume I, 1947–1949.
sufficient experimental sensitivity can be obtained to determine the integrated fractional absorption for log(10.6P_K'X) less than about 0.5, then P_K'X is roughly determined independently of the absolute value of a.

V. INTENSITY ESTIMATES ON SPECTRAL LINES BELONGING TO THE FUNDAMENTAL VIBRATION-ROTATION BAND OF CO

The nonlinear parts of the curves of growth may also be used, in principle, to determine infrared intensities and the line-shape parameter a for lines with Doppler and Lorentz broadening. A graph similar to the one shown in Fig. 1 applies under suitable experimental conditions.

For CO at 300°K the integrated intensity for the rotational line J = 6 → J = 7 belonging to the fundamental vibration-rotation band (n = 0 → n = 1) is found to have the value S = 7.81 cm⁻²·atmos⁻¹. The center of this spectral line occurs at 2169 cm⁻¹.

\[ \log(10.6P_K'X) \approx 1.3 \]

Therefore \[ P_K' = 1.85 \times 10^4 \text{ cm}^{-1} \text{·atmos}^{-1} \]. For \( X_1 = 10^{-4} \text{ cm-atmos} \), \( \log(10.6P_K'X) \approx 1.3 \) and, if \( a \approx 1 \), Fig. 1 applies again for \( X_2 = 3 \times 10^{-3} \text{ cm-atmos} \). If the collision half-width for CO at 300°K and atmospheric pressure is 0.065 cm⁻¹, then \( a \approx 1 \) at a total pressure of about 0.05 atm. It is of interest to note that \( a \approx 20 \) at atmospheric pressure and room temperature for CO.

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**Diffusion Coefficients of Fatty Acids and Monobasic Phosphoric Acids in n-Decane**

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Diffusion coefficients of the series of even-numbered fatty acids from C₆ to C₁₅, of three dialkyl phosphoric acids, and of 2-ethylhexoic and benzoic acids have been measured in dilute solutions in n-decane at 30°C. Gravity mixed diaphragm cells have been employed in making the measurements. The Stokes-Einstein hydrodynamic relationship adjusted by an empirical coefficient represents the magnitude and variation of diffusion coefficients in the series of fatty acids if corrections are made for solute association and nonsphericity. The unmodified Stokes-Einstein equation predicts diffusion coefficients lower than those measured by approximately a factor of two.

Little information exists that relates the diffusion coefficients in a series of materials to a systematic change in molecular structure in the series. Of particular industrial interest are hydrocarbon solutions of alcohols, acids, and soaps. These may range from true solutions exhibiting little association to micellar structures with solute apparent molecular weights in the tens of thousands. In addition to providing information on structure, diffusion coefficients may relate transport rates with concentration gradients in hydrocarbon oils not subject to mechanical mixing. Quasi-static oil layers are encountered at surfaces where rheological considerations require that mechanical flow diminish to zero. With these considerations in mind the diffusion coefficients of a series of typical acids of interest in a selected hydrocarbon oil, decane, have been measured at 30°C; these include the even numbered fatty acids from C₆ to C₁₅, three monobasic phosphoric acids, benzoic acid and 2-ethylhexoic acid.

**DIFFUSION THEORY**

The Stokes-Einstein equation as modified by Perrin¹ for an elongated ellipsoidal geometry of the diffusate molecule has been widely applied to systems where the diffusate molecule is large compared with the solvent molecule:

\[ D = \frac{kT}{6\pi(3/4\pi)^{1/3}} (N/V)^{1/3} f, \]  

¹ F. Perrin, J. phys. radium 7, 1 (1936).