Correction for the Intensities of Infrared Absorption Bands

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(Received January 13, 1958)

The serious disadvantage of infrared absorption spectroscopy is the fact that the band shapes and the peak intensities measured in liquids or in solutions are markedly affected by the spectral slit widths of the spectrometers. Therefore it is desirable to find the method of correction of the apparent peak intensities and the band half widths to the true intensities and half widths, respectively, and to express them with the universal values. A number of authors$^{1-4)}$ have discussed this problem. In the present work we have compared the methods established by these authors from the view points of the spectral slit width, the slit function, and the shape of the absorption band, and have proposed improved methods.

In the last section of this paper, the improved correction method was applied

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1) D. A. Ramsay, *J. Am. Chem Soc.*, **74**, 72 (1952).
2) A. C. Hardy and F. M. Young, *J. Opt. Soc. Am.*, **39**, 265 (1949).
3) R. A. Russell and H. W. Thompson, *Spectrochim. Acta*, **9**, 133 (1957).
4) E. B. Wilson, Jr. and A. J. Wells, *J. Chem. Phys.*, **14**, 578 (1946).

to the C=O stretching vibration bands of fifteen esters in carbon tetrachloride solutions, and the values of the true molecular extinction coefficient were determined. The true integrated absorption intensities per one C=O group were also obtained by the extrapolation method. These values are dispensable for the group type analysis of esters.

Correction for the Peak Intensity. Method I.—For monochromatic radiation, the well known absorption law,

$$I=I_0e^{-\alpha ct} \tag{1}$$

applies, and the true molecular extinction coefficient at the absorption maximum is described as*

$$E_{\max}=\frac{1}{ct}\log_{10}(I_0/I)_{\max} \tag{2}$$

However, in the actual spectrometer, due to the use of finite slit widths, the radiation is not monochromatic, and the energy from the exit slit of a spectrometer set at a frequency ν' may be expressed by an energy distribution function $g(\nu,\nu')$**. Accordingly when the spectrometer is set at frequency ν', the apparent intensities of the incident and transmitted radiation are described as

$$\begin{aligned} T_0&=\int I_0(\nu)g(\nu,\nu')\mathrm{d}\nu \\ T&=\int I(\nu)g(\nu,\nu')\mathrm{d}\nu \end{aligned} \tag{3}$$

and the apparent molecular extinction coefficient is given by

$$E^a{}_{\max}=\frac{1}{ct}\log_{10}(T_0/T)_{\max} \tag{4}$$

In the actual prism spectrometer, the observed absorbances $[\log_{10}(T_0/T)=D]$ at the band peaks are markedly affected by the spectral slit widths and are very different from the true values $[\log_{10}(I_0/I)]$.

One of the well known method to correct the apparent absorbance at the band maximum for the true absorbance is proposed by Ramsay¹⁾. Under the following assumptions as,

i) the slit function may be represented by a triangle whose base length is equal to the twice the spectral slit width s,

ii) spectral slit width s is the sum of the term s_1 represents the contribution from the finite mechanical slit width and the term s_2 responsible for the finite resolving power of the prism, and the values of each term are evaluated by the equation given by Williams⁵⁾,

iii) the true band shape may be represented by a Lorentz curve,

$$\log_e(I/I_0)=\frac{a}{(\nu-\nu_0)^2+b^2} \tag{5}$$

Ramsay has computed the apparent band absorbance

$$\log_{10}(T_0/T)_\nu=\log_{10}\int g(\nu,\nu')\mathrm{d}\nu$$
$$-\log_{10}\int g(\nu,\nu')\cdot\exp\left(\frac{-a}{(\nu-\nu_0)^2+b^2}\right)\mathrm{d}\nu \tag{6}$$

and obtained the relationships between the ratio of the true and apparent peak intensities and the ratio of the spectral slit widths to the band half widths.

However, Ramsay's assumption is not applicable to every case, and it is necessary to reexamine it. Ignoring the diffraction by a prism, the slit function for a perfectly aligned spectrometer with an equal entrance and exit slit width may be represented by a triangle as described by Ramsay. But owing to the mismatching of the curved image of the entrance slit with the exit slit curvature, the misfocusing of the collimator mirror, etc., for the spectrometer which we actually used, the slit widths of the entrance and exit slits are not equal, and therefore the shape of the slit function may be approximated more closely to trapezoid than to triangle.

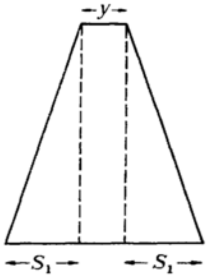

Fig. 1. Trapezoidal slit function.

Then the spectral slit width itself is rewritten as

$$s=s_1+s_2+s_3 \tag{7}$$

where s_1 and s_2 are the same as defined by Ramsay and s_3 is the term represents the contribution from opical misalignment. The details of the trapezoidal slit function illustrated in Fig. 1 are

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* In this equation c is expressed moles per liter of solution and t is the cell length in cm.

** This function is defined as the slit function.

5) V. Z. Williams, *Rev. Sci. Instrumensts*, **19**, 151 (1948).

TABLE I-1

VALUES OF $\log_{10}(I_0/I)_{\max}/\log_{10}(T_0/T)_{\max}$ FOR THE VARIOUS VALUES OF y IN TERMS OF THE RATIO OF $s_1+y/\Delta\nu^a{}_{1/2}$*

	$\log_{10}(I_0/I)_{\max}/\log_{10}(T_0/T)_{\max}$									
$s_1+y/\Delta\nu^a{}_{1/2}$	0.15	0.20	0.25	0.30	0.35	0.40	0.45	0.50	0.55	0.60
for $y'=0.000$**	1.016	1.028	1.046	1.066	1.095	1.131	1.176	1.229	1.308	1.416
for $y'=0.025$	1.013	1.025	1.041	1.061	1.088	1.124	1.167	1.220	1.295	1.396
for $y'=0.050$	1.011	1.022	1.037	1.057	1.082	1.116	1.158	1.210	1.283	1.378
for $y'=0.075$	1.011	1.019	1.033	1.052	1.076	1.108	1.150	1.200	1.270	1.364
for $y'=0.100$	1.009	1.017	1.030	1.049	1.072	1.102	1.139	1.188	1.255	1.345
for $y'=0.125$	1.009	1.016	1.028	1.045	1.066	1.095	1.133	1.180	1.245	1.330

* This Table can be applied to the values of $\log_{10}(T_0/T)_{\max}$ from 0.2 to 0.4.

** The value of y' is defined as $y/\Delta\nu^t{}_{1/2}$.

TABLE I-2

VALUES OF $\Delta\nu^a{}_{1/2}/\Delta\nu^t{}_{1/2}$ FOR THE VARIOUS VALUES OF y IN TERMS OF $\log_{10}(T_0/T)_{\max}=D_{\max}$ AND THE RATIO OF $s_1+y/\Delta\nu^a{}_{1/2}$

	$\Delta\nu^a{}_{1/2}/\Delta\nu^t{}_{1/2}$									
$s_1+y/\Delta\nu^a{}_{1/2}$	0.15	0.20	0.25	0.30	0.35	0.40	0.45	0.50	0.55	0.60
for $y'=0.000$										
$D_{\max}=0.2$	1.021	1.038	1.060	1.091	1.131	1.180	1.242	1.320	1.422	1.550
$=0.3$	1.020	1.036	1.058	1.087	1.125	1.172	1.228	1.302	1.398	1.525
$=0.4$	1.020	1.035	1.056	1.084	1.120	1.165	1.218	1.284	1.372	1.485
for $y'=0.025$										
$D_{\max}=0.2$	1.018	1.034	1.054	1.084	1.122	1.168	1.229	1.304	1.402	1.528
$=0.3$	1.018	1.032	1.053	1.081	1.117	1.162	1.216	1.287	1.380	1.502
$=0.4$	1.018	1.031	1.051	1.078	1.112	1.154	1.206	1.272	1.358	1.472
for $y'=0.050$										
$D_{\max}=0.2$	1.015	1.030	1.050	1.078	1.113	1.159	1.216	1.290	1.384	1.510
$=0.3$	1.015	1.029	1.047	1.074	1.108	1.152	1.204	1.273	1.362	1.482
$=0.4$	1.015	1.027	1.045	1.071	1.103	1.144	1.195	1.258	1.343	1.452
for $y'=0.075$										
$D_{\max}=0.2$	1.013	1.027	1.047	1.074	1.106	1.149	1.204	1.274	1.365	1.490
$=0.3$	1.013	1.026	1.045	1.070	1.102	1.142	1.193	1.259	1.348	1.465
$=0.4$	1.013	1.025	1.043	1.067	1.097	1.134	1.181	1.246	1.330	1.437
for $y'=0.100$										
$D_{\max}=0.2$	1.012	1.024	1.042	1.066	1.098	1.138	1.191	1.262	1.348	1.472
$=0.3$	1.012	1.023	1.040	1.063	1.094	1.132	1.182	1.246	1.332	1.445
$=0.4$	1.012	1.022	1.039	1.061	1.090	1.128	1.175	1.234	1.314	1.415
for $y'=0.125$										
$D_{\max}=0.2$	1.010	1.022	1.039	1.063	1.094	1.134	1.182	1.248	1.332	1.445
$=0.3$	1.010	1.021	1.037	1.059	1.088	1.124	1.172	1.233	1.314	1.425
$=0.4$	1.010	1.020	1.035	1.056	1.083	1.118	1.162	1.220	1.296	1.395

defined as follows. The length of the upper side is equal to the sum of s_2+s_3 and denoted as y, and the lower base length is equal to $2s_1+y$. This slit function is regarded as the combination of the triangular slit function whose base length is equal to twice the term which represents the contribution from the finite mechanical slit width, and the rectangular slit function whose base length is equal to the term which is responsible for the prism diffraction and the optics misalignment.

Using the trapezoidal slit function as defined above, Eq. 6 was evaluated by numerical integration, for the various values of a, b, and the slit widths s_1 and y. For the stepwise increment of the value of y, the ratios of $\log_{10}(I_0/I)_{\max}/\log_{10}(T_0/T)_{\max}$ and $\Delta\nu^a{}_{1/2}/\Delta\nu^t{}_{1/2}$ were represented as functions of the apparent intensities and of the ratio $s/\Delta\nu^a{}_{1/2}$. The results are given in Table I, and the rows for $y=0$ are the same as given by Ramsay.

With this Table we can correct the observed intensities and band half widths to true ones, but it is necessary to determine the value of y experimentally, since the value of y is not known a priori. For this purpose, the absorption measurements of the same sample are made with the various mechanical slit widths, and one set of observed values for the peak intensities and band half widths are obtained. Then assuming an arbitrary y value, the spectral slit width s is determined, and the correction factor for the peak intensities observed by that slit width is found from Table I-1. Using the same y value, the similar processes are tried for the values observed with the other mechanical slit widths. If we assume an unsuitable y value, the corrected peak intensities for the various mechanical slit widths should not agree, and the similar calculations with the another y values must be repeated until we get the satisfactory agreement among the corrected intensities. The corrected peak intensities which finally agree may be considered as the true peak intensities. For the observed band half widths, the similar treatments should be made by the use of Table I-2, and the band half widths are also corrected.

This method is applied to the C=O stretching vibration bands of ethyl capronate measured in carbon tetrachloride solution, and illustrated in Table II. The corrected peak intensities show always good agreement, when we assume the value of y to be ca. 1.6 cm^{-1}. (In Table I, the correction factors are represented as the functions of $y'=y/\Delta\nu^t{}_{1/2}$ and in this case $\Delta\nu^t{}_{1/2}$ is nearly equal to 16 cm^{-1}, therefore, we get a good agreement with the value of $y'=0.1$). Therefore, when the intensity measurement in the 1700 cm.$^{-1}$ region is made with the same spectrometer under the same condition of alignment, the value of y should be always assigned to ca. 1.6 cm^{-1}*, but the value of y' should be altered according to the band half widths. In Table II, the result obtained from Ramsay's method is compared with the result of ours. The more excellent agreement among the corrected intensities is obtained with our method. The reliability of our method is also proved from the agreement between the observed resolution and the spectral slit width, and the equality between the corrected intensities and the intensities measured with a grating spectrometer under the higher resolution.

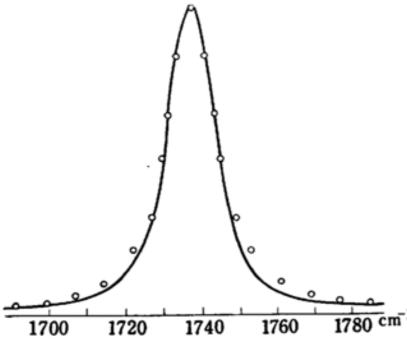

Fig. 2. Comparison between the observed and the calculated absorbance.

The aforementioned correction method is derived from the Lorentz curve approximation for the true band shape. To examine this assumption, the results of numerical integration of Eq. 6 are compared with the observed absorption curves of ethyl capronate in carbon tetrachloride solution. The results are shown in Fig. 2, where the full line represents the observed absorbance curve and the dots represent the calculated values.

The agreement between these curves is well in the central region of the bands and in the band wings, but in the middle of these regions, comparatively large differences are observed. An exponential curve, which is used by Philpotts⁶⁾ for the band shape, is also examined, but the calculated points markedly deviate from the observed curves except in the narrow central region of the bands. Therefore, for the correction of the observed peak intensities and the band half widths, it is considered to be reasonable to assume Lorentz curve for the true band shape.

Correction for the Peak Intensity. Method II.—Koana⁷⁾ and Hardy²⁾ showed the other correction method. For the symmetrical bands, the corrected absorbance at the band maximum ($D^0{}_{\max}$) is represented as a first approximation by the

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* The value of s_3 which represents the contribution from the misalignment of optics is nearly equal to 1.2 cm^{-1} (=1.6−0.4 cm^{-1}). This value is surprisingly large, but after the readjustment of optics, the value of s_3 was diminished to ca. 0.4 cm^{-1}.

6) A. R. Philpotts, W. Thain and P. G. Smith, *Anal. Chem.*, **23**, 268 (1951).

7) K. Koana, et al., *Proc. Phys.-Math. Soc. Japan*, (*Nippon Sugaku-Butsuri Gakkaishi*) **22**, 940 (1940).

TABLE II

CORRECTION FOR THE INTENSITIES (METHOD I) ETHYL CAPRONATE IN CARBON TETRACHLORIDE CONCENTRATION 0.044 mol./l. PATH LENGTH 0.124 mm. BAND AT 1737 cm^{-1}

mechanical slit width mm.	0.13	0.17	0.23	0.29	0.225*
s_1 cm^{-1}	1.43	1.87	2.53	3.19	1.0 *
observed $D_{\max}$	0.327	0.326	0.324	0.318	0.332*
$\Delta\nu^a{}_{1/2}$ cm^{-1}	15.6	15.7	16.0	16.2	15.5 *
for $y/2b_0=0.025$					
s_1+y cm^{-1}	1.82	2.26	2.92	3.58	
corrected $D_{\max}$	0.330	0.330	0.331	0.328	
for $y/2b_0=0.05$					
s_1+y cm^{-1}	2.21	2.65	3.31	3.97	
corrected $D_{\max}$	0.330	0.331	0.332	0.329	
for $y/2b_0=0.075$					
s_1+y cm^{-1}	2.58	3.02	3.68	4.34	
corrected $D_{\max}$	0.332	0.332	0.333	0.331	
for $y/2b_0=0.10$					
s_1+y cm^{-1}	2.96	3.40	4.06	4.72	
corrected $D_{\max}$	0.332	0.333	0.334	0.332	
for $y/2b_0=0.125$					
s_1+y cm^{-1}	3.33	3.77	4.43	5.09	
corrected $D_{\max}$	0.334	0.335	0.336	0.335	
for $y/2b_0=0.0$					
$s_1+0.4$** cm^{-1}	1.83	2.27	2.93	3.59	
corrected $D_{\max}$	0.331	0.331	0.332	0.329	

* These values are measured with a P-E. 112G grating spectrometer.

** These values are obtained using a triangular slit function, the term s_2 responsible for the finite resolving power of the prism is equal to 0.4 cm^{-1}.

TABLE III

CORRECTION FOR THE PEAK INTENSITIES (METHOD II) ETHYL CAPRONATE IN CARBON TETRACHLORIDE. CONCENTRATION 0.044 mol./l. PATH LENGTH 0.124 mm. BAND AT 1737 cm^{-1}

mechanical slit width mm.	0.13	0.17	0.23	0.29
s_1 cm^{-1}	1.43	1.87	2.53	3.19
observed $D_{\max}$	0.327	0.326	0.324	0.318
observed $D''_{\max}$	−0.009	−0.009	-0.008_5	-0.008_5
for $y=0.0$ cm^{-1}*				
coefficient a_2	0.279	0.428	0.715	1.074
corrected $D_{\max}$	0.330	0.330	0.330	0.327
for $y=1.2$ cm^{-1}				
coefficient a_2	0.373	0.539	0.847	1.226
corrected $D_{\max}$	0.330	0.331	0.331	0.328
for $y=1.6$ cm^{-1}				
coefficient a_2	0.468	0.648	0.978	1.380
corrected $D_{\max}$	0.331	0.332	0.332	0.330
for $y=2.0$ cm^{-1}				
coefficient a_2	0.575	0.770	1.123	1.545
corrected $D_{\max}$	0.332	0.333	0.334	0.331

* These values are obtained using a triangular slit function, the term s_2 responsible for the finite resolving power of the prism is equal to 0.4 cm^{-1}.

TABLE IV

ESTER C=O BANDS IN CARBON TETRACHLORIDE SOLUTION

Compounds	$\nu_{\max}$ (cm^{-1})	$E_{\max}$ (l/mol. cm.)	$\Delta\nu^t_{1/2}$ (cm^{-1})	$A\times10^8$ (cm^2/molecule. sec.)
methyl formate	1735	730	10.5	142
methyl acetate	1748	715	12.6	143
ethyl acetate	1742	732	12.7	149
n-butyl acetate	1741	590	15.9	151
isoamyl acetate	1742	605	15.7	156
ethyl propionate	1739	560	15.6	137
ethyl capronate	1737	615	15.6	147
dimethyl oxalate	1752	1050	9.5	268
	1781	570	9.8	
diethyl oxalate	1747	1010	11.6	291
	1773	540	12.5	
diethyl malonate	1739	825	15.6	302
	1756	630	16.7	
diethyl succinate	1739	1180	15.7	285
di-2-ethylhexyl adipate	1737	1090	17.5	307
di-2-ethylhexyl azelate	1736	1130	17.2	325
di-2-ethylhexyl sebacate	1736	1130	17.0	297
diethyl maleate	1735	1000	20.0	302

observed absorbance and its second derivative, i. e.,

$$D^0_{\max}=D_{\max}-a_2(\mathrm{d}^2D/\mathrm{d}\nu^2)_{\max} \qquad (8)$$

where a_2 is a coefficient determined by the slit function, and given by

$$a_2=\frac{\int g(\nu,\nu')\nu^2\mathrm{d}\nu}{\int g(\nu,\nu')\mathrm{d}\nu} \qquad (9)$$

The a_2 values* are represented for the cases of a triangular slit function whose base length is equal to twice the spectral slit width s as $s^2/12$, and for a trapezoidal slit function whose details are defined in the preceding section as $[(s_1+y/2)^4-(y/2)^4]/12s_1(s_1+y)$.

To obtain the true corrected intensity, the trial and error examination of the value of y should be made in a similar manner as described in the preceding section. An example of this process is carried out for the C=O stretching band of ethyl capronate, and shown in Table III, where the third and fourth rows show the observed peak intensities and their second derivatives, respectively. The good agreement among the corrected intensities is obtained when we assume the value of y to be ca. 1.6 cm^{-1}.

This method is attractive, because of the non-existence of the assumption on the band shape, but the process to obtain the second derivatives of absorbances is troublesome. Moreover, Eq. 8 is only a first approximation, and for the large values of absorbances, Eq. 8 should be extended to the fourth derivative. These two disadvantages are too serious, and in the last section of this paper this method is not adopted.

True Integrated Absorption Intensity.—As regards the integrated intensities, there are few to be discussed, and the extrapolation method proposed by Wilson and Wells3) can be applied to the actual cases. Namely, true integrated intensity A is obtained as the limiting value of the intensity B, i. e.,

$$A=\lim_{ct\to0}B=\lim_{ct\to0}\frac{1}{ct}\int\log_e(T_0/T)\mathrm{d}\nu \qquad (10)$$

where c is the concentration of the solute in molecules per cm.^{3} of solution, t is the cell length in cm., and ν is the frequency in cycles per second. Integration of the band is carried out over the frequency interval of the four times the apparent band half width on either sides of the band center. Special correction for the residual area under the wings is ignored.

Results on the C=O Band of Esters.—Table IV gives the frequencies of the band maxima, the true molecular extinction coefficients at the peak, the true band half widths, and the true integrated absorption intensities of C=O stretching vibration bands of fifteen esters as measured in carbon tetrachloride solutions. These results show good agreement with the

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* In the original paper2), a_2 is determined experimentally. But this procedure is quite erroneous, and here a_2 is calculated from the assumed slit function.

values obtained by the other authors[8-10].

The mean values and their standard deviations of the peak and area intensities per one C=O group are computed for the seven monoesters as

$$(E_{\text{group}})_{\max}=647\pm73 \quad \text{l.mol.}^{-1}\text{cm.}^{-1},$$

$$A_{\text{group}}=146.4\pm6.3\times10^{-8} \quad \text{cm}^2\,\text{molecule}^{-1}\,\text{sec.}^{-1},$$

and the mean value of area intensities per one C=O group for the fifteen mono- and di-esters is given by

$$A_{\text{group}}=147.5\pm6.2\times10^{-8} \quad \text{cm}^2\,\text{molecule}^{-1}\,\text{sec.}^{-1}$$

The mean values of area intensities per one C=O group are similar for the mono- and di-esters, and in both cases, the standard deviations of area intensities are quite small. This fact is valuable for the group type analysis of esters.

Experimental

A Perkin-Elmer Model 112 spectrometer with calcium fluoride prism and a cell of 0.124 mm. thickness, determined by the interference method, was employed. All of the esters were purified by the ordinary method and distilled. The boiling points of the purified materials were in good agreement with the literature values.

We wish to express our sincere thanks to Professor S. Mizushima and Assistant Professor T. Shimanouchi who permitted us to use the grating spectrometer.

The cost of this work has been partly defrayed by a grant from the Ministry of Education.

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[9] G. M. Barrow, *J. Chem. Phys.*, **21**, 2008 (1953).

[10] S. A. Francis, ibid. **19**, 942 (1951).