

A Simplified Method of Calculating Absorbed Intensity in Photometric Experiments

R. E. Hunt and Terrell L. Hill

Citation: *The Journal of Chemical Physics* **15**, 111 (1947); doi: 10.1063/1.1746422

View online: <http://dx.doi.org/10.1063/1.1746422>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/15/2?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[The Calculation Of Absorbing Thin Film Optical Constants And Electronic Structure From Photometric Measures On Domain IRVISUV Using Neural Networks](#)

AIP Conf. Proc. **1047**, 284 (2008); 10.1063/1.2999959

[A simplified Fourier series method for the calculation of magnetostatic interactions in bubble circuits](#)

AIP Conf. Proc. **29**, 44 (1976); 10.1063/1.30386

[Calculation of Infrared Intensities by the CNDO Method](#)

J. Chem. Phys. **47**, 4236 (1967); 10.1063/1.1701605

Photometrics

Phys. Today **3**, 22 (1950); 10.1063/1.3066711

[A Model Method of Photographic and Photometric Determination of Heat Radiation Between Surfaces and Through Absorbing Gases](#)

J. Appl. Phys. **13**, 246 (1942); 10.1063/1.1714862



Letters to the Editor

THIS section will accept reports of new work, provided these are terse and contain few figures, and especially few halftone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section should not exceed 600 words in length and must reach the office of the Managing Editor not later than the 15th of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual publication charge (\$3.00 per page) will not be made and no reprints will be furnished free.

A Simplified Method of Calculating Absorbed Intensity in Photometric Experiments

R. E. HUNT AND TERRELL L. HILL
Department of Chemistry, University of Rochester, Rochester, New York
January 10, 1947

IN studying photochemical reactions it is frequently necessary to calculate the intensity of absorbed radiation from measurements of the transmitted intensity. The usual method is an approximate one and involves calculation of the fraction of light reflected and re-reflected from each interface of the cell windows, and then the amount of this reflected radiation actually absorbed by the gas in question. These corrections are continued until the desired degree of accuracy is obtained. Much of the tedious computation may be avoided by using instead a treatment which is exact within the limits of the assumptions made.

Let us assume that a parallel beam of light is incident upon the front (optically plane) window of a reaction vessel and that it passes through the vessel and out the rear window where it is then completely captured by a photo-cell, thermopile or actinometer. Examining for the moment of a single window, a certain fraction (f) of the light incident upon any interface will be reflected. A certain small fraction will be absorbed by the window itself and lost. This may be combined with the fraction lost due to scattering by the surface and by imperfections in the window itself, and the total represented by w . The situation then for each window is shown in Fig. 1. Summing up the two infinite series representing total radiation reflected (R) and transmitted (T), and putting them in the form $1/1-x$, we obtain

$$R = f + \frac{(1-f)^2 f (1-w)^2}{1 - (1-w)^2 f^2}, \quad (1)$$

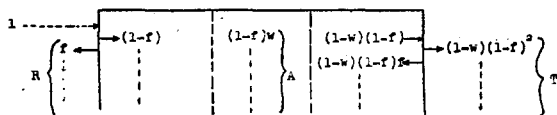


FIG. 1. Radiation reflected, absorbed, and transmitted by a single window.

$$T = \frac{(1-w)(1-f)^2}{1 - (1-w)^2 f^2}. \quad (2)$$

Also, $R + T + A = 1$, where A is the total radiation absorbed and scattered.

We now consider the cell as a whole, with two such windows separated by a column of absorbing gas. Let α be the fraction of radiation which is absorbed in a single passage through the gas column. Let us assume also that the windows are identical in behavior. This situation may be pictured as in Fig. 2. Again summing separately the terms representing radiation reflected from the front of the cell, absorption by the gas column, and radiation transmitted at the rear of the cell, we obtain in a similar manner

$$\frac{I_a}{I_0} = \frac{T\alpha}{1 - R(1-\alpha)}, \quad (3)$$

$$\frac{I_t}{I_0} = \frac{T^2(1-\alpha)}{1 - (1-\alpha)^2 R^2}. \quad (4)$$

Here I_a and I_t are the absorbed (by the gas) and transmitted intensities, and I_0 is the incident intensity striking the front window. With the cell evacuated, α in Eq. (4) becomes zero, yielding a relation between incident intensity and that transmitted by the empty cell (I_t^0):

$$I_t^0/I_0 = T^2/(1-R^2). \quad (5)$$

T , R , and w may then be found from Eqs. (1), (2), and (5), using a value of f calculated from Fresnel's law for reflection at an interface, and inserting the measured values of I_0 and I_t^0 . For a good grade of fused quartz and an evacuated cell ($f=0.038$), the values of R and T turn out to be about 0.07 and 0.91, respectively, and w comes out somewhat smaller than f .

The complete procedure in principle is the following: calculate R , T , and w as indicated above; then employing these values of R and T and an experimental value of I_t/I_0 , α is found from Eq. (4); finally, α , R , and T are substituted into Eq. (3) to give I_a/I_0 . However, in practice, we may neglect, to a good approximation (about 0.5 percent, or less), R^2 and f^2 compared to unity in Eqs. (1), (2), (4), and (5), and obtain

$$R = f + (1-f)^2 f (1-w)^2, \quad (1')$$

$$T = (1-w)(1-f)^2, \quad (2')$$

$$I_t/I_0 = T^2(1-\alpha), \quad (4')$$

$$I_t^0/I_0 = T^2. \quad (5')$$

These simplified equations may now easily be combined to give α , R , and T as explicit functions of the experimental quantities f , I_t/I_0 , and I_t^0/I_0 . Substituting these expressions for α , R , and T into Eq. (3), we have the final result

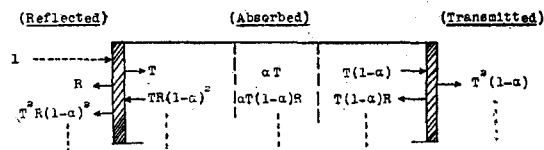


FIG. 2. Radiation reflected, absorbed, and transmitted by a cell with plane parallel windows, which contains a substance absorbing (in a single passage) a fraction α of the light incident upon it.

$$\frac{I_a}{I_0} = [(I_t^0/I_0) - (I_t/I_0)] \times \frac{(I_t^0/I_0)^{\frac{1}{2}}}{(I_t^0/I_0) - f \left[1 + \frac{(I_t^0/I_0)}{(1-f)^2} \right] (I_t/I_0)} \quad (6)$$

It might be pointed out that a method sometimes used in spectrophotometric work for calculating the absorbed intensity—namely, taking the simple difference between transmitted intensity with the cell empty and filled with gas—can introduce a large error. The factor multiplying $(I_t^0/I_0) - (I_t/I_0)$ in Eq. (6), in a typical case (i.e., $I_t^0/I_0 = 0.85$, $f = 0.04$), varies from 1.08 for complete absorption by the gas to 1.17 at zero absorption.

We have referred throughout to absorption by a gas. It is clear that a very similar treatment can be given for a liquid solution.

Polarization of Raman Lines

GEO. GLOCKLER AND JO-YUN TUNG

Department of Chemistry and Chemical Engineering, State University of Iowa, Iowa City, Iowa

December 31, 1946

IN earlier studies of the polarization of Raman lines¹⁻³ we suggested certain arrangements of polaroid films in front of the slit of the spectrograph. At that time we also employed grids to obtain nearly parallel incident light, in order to measure the depolarization factor. In many experiments on the Raman effect it is, however, sufficient to know which of the Raman lines are depolarized without necessarily determining the depolarization factor numerically. We have therefore evolved another experimental set-up as shown in Fig. 1.

Two Raman tubes (*Ra*) are supported by two brass tubes (*B*). These brass tubes carry on the other end two condensing lenses (*Le*). The bottom of the top Raman tube and the top of the bottom Raman tube are both painted with a strip of optical black ($\frac{1}{8}$ " wide) and parallel to the Raman tube axis. This black strip avoids scattered radiation from each Raman tube interfering with the other. The scattered radiation coming through the windows of

the Raman tubes is focused by means of the two lenses (*Le*) (focal length 12.2 cm) onto the slit of the spectrograph. An appropriate diaphragm is placed in front of the slit and the two scattered beams are separated by a blackened metal foil. The distance between the Raman windows and the lenses is 15.3 cm and the distance from the lenses to the double slit is 17.9 cm.⁴ The brass tubes (*B*) are adjusted by six screws each, until the two scattered light beams from the Raman tubes have the same intensity and shape of image when viewed in the spectrograph. One of the Raman tubes is surrounded by a film of polaroid in which the electric vector lies along the axis of the Raman tube, whereas the second Raman tube is wrapped in a piece of polaroid with its electric vector at right angles to the axis of the Raman tube. We used twelve A. H. 2 General Electric Company mercury vapor lamps arranged horizontally in circular fashion, surrounded by a silvered cylindrical metal reflector. This arrangement is somewhat similar to one described by Edsall and Wilson.⁵ Between the Raman tubes and the mercury lamps there is located a water jacket which keeps the heat generated by the lamps from reaching the substance under investigation. The mercury lamps are kept at constant temperature by using a bi-metallic temperature control. Its mercury switch operates the motor of a blower which draws air past the lamps; cooling them. This control is intermittent, but works very satisfactorily. Another blower draws air through the inner region of the water jacket, containing the Raman tubes. By adjusting the speed of this motor, the temperature of the inner region is kept remarkably constant.

We obtain the spectrum of carbon tetrachloride with polaroid films as shown in Fig. 2. With the above-mentioned light sources, the photograph could be taken in four hours' exposure. It is not necessary to use filters. The photographic plates employed were Eastman Kodak 103a-0. By surrounding the two Raman tubes with an appropriate system of metal grids, it should be possible to make the incident light parallel. A numerical measure of the depolarization factor could then be obtained.

An advantage of the new arrangement lies in the fact that current fluctuations affect both Raman tubes in the same way. The qualitative results obtained are sufficient to indicate the depolarized lines.

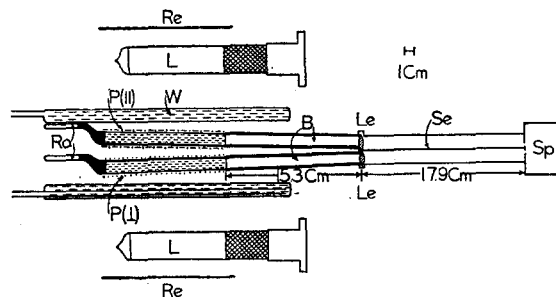


FIG. 1. Raman apparatus. *Re*=reflector, *L*=lamps, *W*=water jacket, *Ra*=Raman tubes, *P*(I), *P*(II)=polaroid films, *B*=brass tubes, *Le*=condensing lenses, *Se*=separating blackened metal sheet, *Sp*=spectrograph.

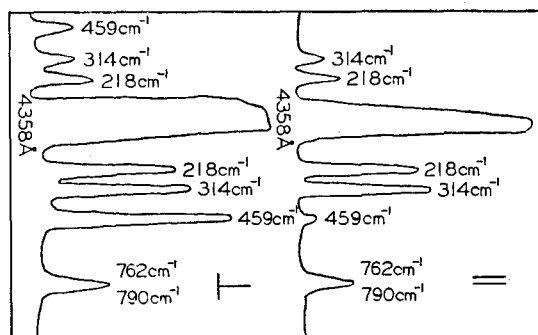


FIG. 2. Microphotograph of CCl_4 spectrum.