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A Single Exposure Photographic Method for Depolarization Factor Measurements*

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A single exposure photographic method for the measurement of depolarization factors in Raman spectroscopy is described. The accuracy of the results was tested by measurements with carbon tetrachloride and chloroform. The depolarization factors found for highly polarized lines were in good agreement with those given by the photoelectric method rather than with those of other photographic investigations.

INTRODUCTION

THE experimental methods for depolarization factor measurements receiving particular attention in recent years have been the two exposure photographic method^{1,2} and the photoelectric technique.³ The latter is especially adapted to measurements on highly polarized lines but its application is difficult with equipment having low light gathering power, and very weak Raman lines would require some integrating method for recording in any event. The disadvantages of the two exposure method, which include errors due to fluctuations in the incident light, progressive sample discoloration and decomposition, and fluctuations in the response of the photographic emulsion caused by changes in temperature and humidity and by decay of the photographic latent image, would seem to outweigh the superiority in speed over a single exposure method, particularly in the usual case where the investigation of a large number of samples in a short time was not

contemplated. The present paper is a report on a modified version of the single exposure method of Reitz⁴ which has yielded satisfactory results.

EXPERIMENTAL DETAILS

Equipment

A schematic diagram of the assembled equipment is given in Fig. 1. To avoid the convergence of the incident light produced by a cylindrical Raman tube, the jacket and tube were made of square cross section in the illuminated region. The internal diameter of the tube proper was approximately 12 mm. Instead of the conventional horn, the back end of the tube was closed by a plane glass window which facilitated alignment of the tube.

Four Type AH-11 mercury vapor lamps were employed for illumination as shown; the bright core of the lamp was approximately three inches from the tube jacket. To define correctly the illuminated area of the tube, a shield of blackened metal was provided which covered the tube completely except for two longitudinal strips three-eighths of an inch wide. This shield also served as a mount for two-inch long blackened metal baffles which could be clipped on at one-quarter inch intervals. Air was circulated by a blower through the transite box which housed the excitation unit.

The filter solution, which consisted of 4 percent paranitrotoluene and 0.03–0.06 percent crystal violet in ethyl alcohol, was circulated from a reservoir where it was maintained at room temperature to eliminate refractive index gradients in the scattering liquid.

Resolution of the scattered light was accomplished by a large aperture (1 sq. in.) 2° quartz Wollaston prism which permitted complete separation of two 3 mm images at the spectrograph slit. A quarter-wave plate was used to convert the resolved, plane-polarized components into circularly polarized beams.

A Steinheil Type GH spectrograph with short ($f/3.5$) focal length optics, and a microphotometer of essentially conventional design were used in all work reported here. The photomultiplier unit employed was identical with one previously described⁵ except for the addition of an electrometer tube input stage to the amplifier section.

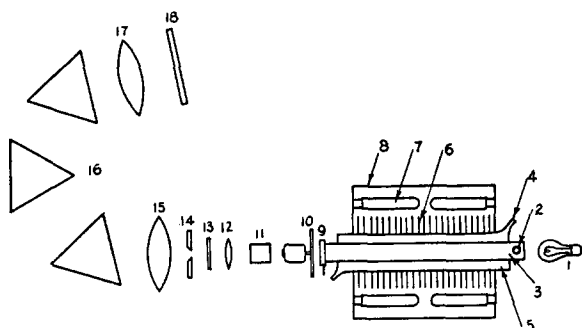


FIG. 1. Schematic diagram of equipment for depolarization factor measurements.

- | | |
|--------------------------|------------------------|
| 1. Lamp | 10. Sector wheel |
| 2. Sample inlet | 11. Wollaston prism |
| 3. Raman tube | 12. Condensing lens |
| 4. Filter solution inlet | 13. Quarter wave plate |
| 5. Filter jacket | 14. Slit |
| 6. Baffles | 15. Collimator lens |
| 7. Lamps | 16. Prisms |
| 8. Housing | 17. Camera lens |
| 9. Iris diaphragm | 18. Plate holder |

* This paper is based on part of a dissertation presented by Philip A. Lyons to the faculty of the graduate school of the University of Wisconsin in partial fulfillment of the requirements for the degree of Doctor of Philosophy in June, 1948.

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¹ F. F. Cleveland, *J. Chem. Phys.* **13**, 101 (1945).

² B. L. Crawford and W. Horowitz, *J. Chem. Phys.* **15**, 268 (1947).

³ A. E. Douglas and D. H. Rank, *J. Opt. Soc. Am.* **38**, 281 (1948).

⁴ A. Reitz, *Zeits. Physik. Chemie* **B33**, 368 (1936).

⁵ J. Y. Chien and P. Bender, *J. Chem. Phys.* **15**, 376 (1947).

Experimental Procedure

After alignment of the Raman tube, the orientation of the quarter-wave plate was changed until the intensities of the resolved components of an unpolarized beam* were equal as measured at the focal plane of the camera lens by the photo-multiplier unit. The apparatus correction usually required to compensate for the differing losses in reflection suffered by the two resolved linearly polarized beams in passage through the spectrograph was thus made negligible. To check the maintenance of this correct setting and to provide for any required correction a photographic record of the resolved components of an unpolarized source was made on each plate on which a Raman spectrum was recorded.

After the Raman exposure was taken plate calibration was carried out with a continuous unpolarized source. A wide range of relative intensities was obtained by use of a sector wheel in conjunction with varying slit widths. The slit had previously been calibrated with the help of the photo-multiplier unit, and the response found to be linear in the range of slit widths employed. Plate calibration curves were prepared by plotting the microphotometer galvanometer deflection *versus* log (relative intensity +1).** Microphotometer tracings of the Raman spectra were obtained, the difference between peak line and background intensities determined for both the \perp and \parallel components, and the depolarization factor calculated for each line in the usual way, the background reading being taken as the interpolated

CCl_4 103 cm^{-1}

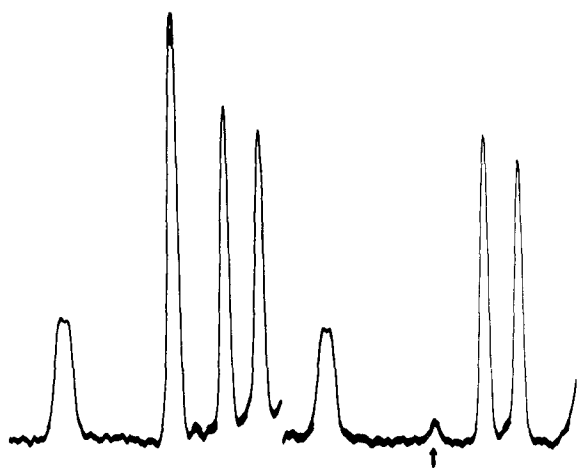


FIG. 2. Densitometer tracings of the \perp and \parallel spectra for carbon tetrachloride.

* Whenever reference is made to an unpolarized light source it will mean a small ground glass screen placed at the front stop of the Raman tube and illuminated from the rear by an incandescent lamp operated from a regulated voltage supply.

** Any arbitrary function of the intensity which would reduce to zero for zero deflection and which when plotted against deflection would be substantially linear over a wide range of densities would be equally convenient.

TABLE I. Depolarization factors for the Raman lines of carbon tetrachloride.

$\Delta\nu$, cm^{-1}	218	314	459	762-790
I	0.90 0.86 0.88 0.83 0.88 0.87	0.88 0.85 0.91 0.84 0.84 0.86	0.02 0.01 0.02 0.03 0.02 0.02	0.90 0.86 0.88 0.84 0.91 0.90
II	0.85 0.84 0.86 0.83 0.80 0.86 0.84 0.85	0.87 0.84 0.83 0.84 0.80 0.86 0.87 0.87		0.88 0.87 0.88 0.90 0.82 0.87 0.89 0.90
III			0.02 0.02 0.02	
Mean	0.85 ₄	0.85 ₄	0.02	0.87 ₈
Av. dev. from mean	0.019	0.020		0.019
Series I: Medium exposure (about 90 minutes). II: Shorter exposure for strong lines. III: Longer exposure for polarized line. Baffle spacing $\frac{1}{4}$ " in all above runs.				

value of the actual background curve at the position of the peak of the Raman line.

Low inertia plates (Types 103a-o and 103a-j) were used. Of a number of developers tested,*** D-91 (a para-aminophenol developer) was chosen as giving lowest fog and grain with fair contrast and without undue loss of emulsion speed. At 18°C a $3\frac{1}{2}$ minute development was used followed by 2-minute washing before fixing.

Experimental Results

Carbon tetrachloride has regularly been employed as a test liquid because it provides a close approach to an absolute standard with which the actual experimental results can be compared. The results of a series of determinations on this compound are given in Table I, while typical microphotometer tracings of the spectra are given in Fig. 2. The accuracy obtained in these cases represents the limiting value available with the technique employed since the measurements were made on lines which were well separated (except for the 762-790 cm^{-1} doublet) and which have a high line to background intensity ratio. Further comparative data on chloroform are listed in Table II.

The effect of the baffle spacing on the results obtained was followed by observations on carbon tetrachloride. The results given in Table III for the 459 cm^{-1} line show clearly that baffles are necessary for accurate measurements on polarized lines.

*** D-11, D-8, D-19, D-76, D-91, DK-60A, Microdol, Edwal 12, and a *p*-phenylene diamine developer were tested.

TABLE II. Depolarization factors for the Raman lines of chloroform.

$\Delta\nu$, cm^{-1}	This research	Douglas and Rank ^a	Crawford and Horowitz ^b
262	0.84		0.86
366	0.14	0.13	0.18
668	0.02	0.026	0.08
760	0.84		0.92
1214	0.9		0.9
3020	0.3		0.4

^a See reference 3.^b See reference 2.

The low value of $\rho=0.02$ found for the $\Delta\nu=459\text{ cm}^{-1}$ line is substantiated by the value of 0.013 recently reported by Douglas and Rank, who have commented on the contrast between this figure and the previously reported values of 0.045 and higher.

DISCUSSION

The most difficult problem in the evaluation of the depolarization factor lies in the correction for the background present. For satisfactory results the background must be low, and of comparable intensity for both components, which requires the use of a source with a low background to line intensity ratio such as the AH-11 (see Fig. 2).

The spectra themselves provide a means for checking the self-consistency of the method of taking background readings. If two lines are depolarized to the limit, ($\rho=6/7$), the ratio of the line intensities for the pair should be the same in both the \perp and \parallel spectra. For the 217 cm^{-1} and 313 cm^{-1} lines of the carbon tetrachloride spectrum such an agreement was actually found, within an average deviation of 1.5 percent, in each of a series of twelve determinations when the aforementioned standard method for background correction was employed. If the background reading was assumed to be the reading at the low wave-number side of the Raman line,² this ratio was slightly higher for the \perp spectrum

TABLE III. Effect of baffle spacing on the depolarization factor for the $\Delta\nu=459\text{ cm}^{-1}$ line of carbon tetrachloride.

Baffle spacing	ρ
$\frac{1}{4}$ "	0.02
$\frac{1}{2}$ "	0.03
1 "	0.05
no baffles	0.10

than for the \parallel spectrum in consequence of the difference in the shape of the background curve in the two spectra.

At least for fairly intense, depolarized lines the limiting accuracy can safely be assumed to be that permitted by the photographic process. The precision of 1.5 percent noted above is somewhat superior to the accuracy achieved in the measurements recorded in Table I. This may be due to reciprocity law failure, to the use of a continuous source for calibration, or to the lack of validity of making background corrections assuming additive intensities. However, since the reciprocity law error results essentially only in a change of the gamma of the calibration curve and since, for the depolarized lines considered, the background and peak line readings correspond to nearly the same positions on the calibration curve for both the \perp and \parallel spectra, reciprocity law failure may be expected to be of secondary importance. Attempts to use neon and argon lamps as line calibration sources were unsuccessful because of fluctuations in the light intensity which occurred in spite of excellent regulation of the lamp power supply.

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