A Raman Apparatus for Quantitative Polarization Measurements

Bryce L. Crawford Jr. and William Horwitz

A Raman Apparatus for Quantitative Polarization Measurements*

Bryce L. Crawford, Jr. and William Horwitz

School of Chemistry, University of Minnesota, Minneapolis, Minnesota

(Received February 26, 1947)

An apparatus for quantitative measurement of the depolarization factors of Raman lines is described. It is a modification of Edsall and Wilson's method, using polaroid cylinders. Short exposure times result from the use of eight exciting lamps. No apparatus corrections are needed. Alignment is not overly critical. Performance is reported on the Raman lines of CCl_4, $CHCl_3$, and C_6H_6.

INTRODUCTION

IT is generally agreed nowadays that no serious study of the Raman spectrum of a molecule is complete without depolarization measurements, at least on the stronger lines. Such information is most helpful in the vibrational analysis, and certainly all possible help is usually needed in establishing an unambiguous vibrational assignment. Moreover, it is worth while to make these measurements *quantitatively;* i.e., so that one obtains numerical values of the depolarization factors rather than a mere labelling of the lines as polarized, partly polarized, or depolarized. In the first place, there are instances in which a clear distinction between complete depolarization ($\rho=0$) and partial depolarization ($\rho<6/7$) enables one to establish the symmetry of the molecule studied. In the second place, numerical values of the depolarization factor give a much better sense of the reliability of the result; the very real difference between the results $\rho=0.40$ and $\rho=0.70$ is lost in the lumping together of such results as "partly polarized."

At the same time, in seeking to design equipment for quantitative polarization measurements, one must not lose sight of the fact that the primary need in Raman spectroscopy is a high intensity of illumination. Also, since the Raman effect is essentially a simple experiment, it is well to avoid complicated apparatus or set-ups involving delicate alignment.

The scheme we have used for Raman observa-tion seems to us to combine rather satisfactorily the desirable qualities of intense illumination, insensitivity to alignment, and good quantitative measurement of the depolarization factors. It is a modification of the first method of Edsall and Wilson.[1] In this paper we shall describe our apparatus, give data on its performance, and list some of its defects which we are planning to improve.

METHODS OF DEPOLARIZATION MEASUREMENT

Methods for measuring depolarization factors fall naturally into two types: those involving a single Raman exposure and those involving two exposures. In the single-exposure apparatus, the scattering substance is illuminated in a single plane by parallel radiation, and the scattered light is observed in a direction strictly perpendicular to the incident light. Deviations from this requirement of perpendicularity give rise to "convergence error." The beam of scattered light is resolved into its two polarized component beams which are slightly separated spatially. Preferential reflection of the polarized beams at optical surfaces (apparatus error) must be eliminated, usually by depolarizing the component beams; finally the component beams are recorded simultaneously, one above the other, on the photographic plate. In the double-exposure method, the two polarized beams are obtained in two successive exposures, with a rotation of some part of the apparatus (lamp, nicol prism, or polaroid) through 90° between exposures.

Of the earlier apparatuses, some of which have been described by Glockler and Baker,[2] those of

[1] J. T. Edsall and E. B. Wilson, Jr., J. Chem. Phys. 6, 124 (1938).
[2] G. Glockler and H. T. Baker, J. Chem. Phys. 11, 446 (1943).

Cabannes and Rousset,[3] and of Reitz[4] stand out as being constructed with elaborate precautions to eliminate possible sources of error. Indeed, these arrangements are often referred to as "ideal." These were both of the single-exposure type, as are most of the more recent arrangements. Glockler and Baker[2] used a split-field polaroid, backed by half-wave mica plates for the component resolution and depolarization. The half-wave plates were later eliminated[5] by placing the resolving polaroids in such a manner that their line of contact was 45° off the vertical axis of the spectrograph. Cleveland[6] also used a split-field polaroid for the resolution but did not depolarize the resolved components. Empirically determined factors were applied to the observed data to correct for the apparatus and convergence errors. A double-exposure apparatus, with polaroid as the resolving element, was described by Rank, Pfister, and Grimm[7] in connection with the application of their photoelectric technique to the measurement of depolarization factors of Raman lines; they also used empirical correction factors.

The single-exposure methods of obtaining depolarization factors have the obvious inherent advantage of being independent of changes in the experimental conditions during a run. Because of theoretical considerations, the exciting radiation must be confined to a single plane. Therefore a maximum of two lamps can be used with this type of apparatus. This condition seriously limits the speed of the apparatus, and, as a rule, relatively long exposure times are required for the polarization spectra. Further, very precise alignment of the Raman tube, lamps, and optical components is necessary, and the Raman tube window must be strain-free. For example, Reitz reported that after several months of use his apparatus showed a residual apparatus correction of 1.065 (instead of 1.000) which was traced to the warping of a wooden support.

A double-exposure apparatus is usually simpler and requires a less critical alignment of parts than a single-exposure arrangement. If polarized light is used for the excitation, lamps can be arranged axially around the Raman tube so that their number and intensity are limited only by the physical dimensions of the lamps and the apparatus (and by the laboratory's facilities for supplying electrical power and for dissipating heat). While one must guard against the danger of conditions changing from the first to the second exposure, improvements in the control of high-intensity mercury lamps to provide intensity stability have advanced to a point where the double-exposure method can compete successfully in accuracy with the single-exposure method.

The possibility of obtaining high incident intensity and relatively short exposure times, was the major consideration which led us to the construction of our double-exposure apparatus.

APPARATUS

Our apparatus is, as mentioned above, a modification of that used by Edsall and Wilson.[1] In their apparatus, they used a cylindrical "light furnace" in which the Raman tube was surrounded by four symmetrically placed mercury arcs; in this manner the radiation field in which the Raman tube was immersed was axially symmetric. In one exposure, the Raman tube was surrounded by a cylinder of polaroid with its optical axis parallel to that of the Raman tube; thus the axially symmetric radiation field was composed of polarized light, the planes of vibration passing through the Raman tube axis. For the comparison exposure, no Polaroid was used and the intensity of the lamps was reduced to provide an approximately correct comparison for the depolarized lines. Edsall and Wilson, of course, intended their set-up only for qualitative polarization studies; for quantitative purposes, it is better to make the comparison exposure using tangentially polarized illumination. The suggestion of using appropriately oriented Polaroid on both exposures was again made by Cleveland and Murray[8] in their discussion of the method of Edsall and Wilson. This suggestion corresponds essentially to our design.

[3] J. Cabannes and A. Rousset, Ann. de physique [X] 19, 229 (1933).

[4] A. W. Reitz, Zeits. f. physik. Chemie B33, 368 (1936); B38, 275 (1937).

[5] G. Glockler, J. F. Haskin, and C. C. Patterson, J. Chem. Phys. 12, 349 (1944).

[6] F. F. Cleveland, J. Chem. Phys. 13, 101 (1945).

[7] D. H. Rank, R. J. Pfister, and H. H. Grimm, J. Opt. Soc. Am. 33, 31 (1943).

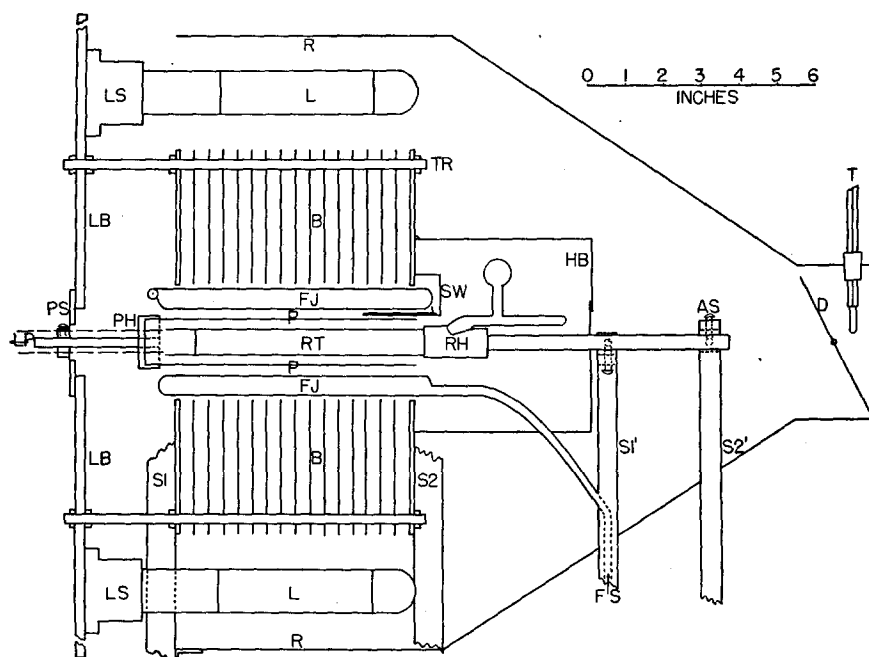[8] F. F. Cleveland and M. J. Murray, J. Chem. Phys. 7, 396 (1939).

FIG. 1. Side view of the Raman apparatus.

AS	Alignment screws	PS	Polaroid holder support
B	Baffles	R	Reflector
BB	Base board	RH	Raman tube holder
D	Damper	RT	Raman tube
FJ	Filter jacket	S1	
FS	Filter solution inlet	S2	Illuminator supports
HB	Hinged box	S1'	
L	Lamp	S2'	Raman tube holder supports
LB	Lamp board	SW	Thermal safety switch
LP	Light path	T	Thermometer
LS	Lamp socket	TR	Tie rods
P	Polaroid	TS	Tripod adjustment screws
PH	Polaroid holder		

The general outline of our apparatus is shown in side and rear views in Figs. 1 and 2. Like Edsall and Wilson, we use a cylindrical light furnace with appropriate baffles and filters. For polarization measurements, we take two exposures. In the first, the Raman tube is surrounded by a cylinder of polaroid with its axis parallel to that of the Raman tube; in the second, a cylinder of polaroid is used with its axis tangentially around the Raman tube.

If we denote the intensities of a given Raman line in the first and second exposures by $I_{\shortparallel}$ and $I_{\perp}$, respectively, then, as Edsall and Wilson discussed, the ratio $(I_{\shortparallel}/I_{\perp})$ is equal to the depolarization ratio ρ as usually defined, with values between 0 and 6/7. Since the beam of scattered light is not polarized, no apparatus correction need be made. We calculated our "convergence error" by an appropriate modification of the method of Gans;[9] with the baffles we use, the correction to be subtracted from the observed ρ is not over 0.01, and accordingly it was neglected.

Spectrograph

A three-prism $f:3$, Steinheil spectrograph, having a dispersion of 32A/mm at 4358A, was used with this apparatus. The resolution at the usual slit width of 0.1 mm was such that the carbon tetrachloride doublet at 762–790 cm^{-1} was just resolved.

Illuminator

The cylindrical illuminator or light furnace contains the baffles and filter jacket. The cham-

[9] Gans, Physik. Zeits. 28, 661 (1927); also in Bhagavantam, *Scattering of Light and the Raman Effect*, Waltair, 1940, Appendix II.

ber inside the jacket contains the polaroid filter, Raman tube, and a bimetallic safety switch which, operating through a relay, will open the lamp circuit if the jacket chamber becomes too warm. The illuminator is connected by a cone-shaped adapter to a blower which ejects the hot air from the room. The damper is placed just in front of the blower, together with a thermometer for indicating the air-stream temperature. The adapter chamber also contains supports for the Raman-tube holder and a hinged, insulated box which keeps the hot air and stray light from entering the center portion of the apparatus. The reflector and the adapter are split along a horizontal diameter for easy access to the interior in changing Raman tubes and in making alignment adjustments.

Lamps

Eight General Electric type A-H2 (250 watt) mercury lamps arranged in a circle and backed by a chromium-plated reflector provide the exciting illumination. These are very intense, self-starting lamps, operating off the usual a.c. power lines through auto-transformers. They have the disadvantages that the mercury spectrum is accompanied by a moderate continuous background in the neighborhood of 4358A,[10] and that the intensity is somewhat sensitive to voltage and temperature fluctuations. Polarization exposures were run at times of day when the line voltage was expected to be rather constant. The lamp temperatures were controlled by a manually operated damper in the cooling air stream. Very little attention was required to maintain the air temperature within plus or minus one degree after an initial half-hour warm-up period. Figure 3 shows the intensity variation of the lamps in density units per minute when the apparatus is uncontrolled (U), and controlled by the damper (C), after an initial warm-up period. It was obtained by taking successive Raman exposures of short duration, and plotting the resulting density per minute of a Raman line against the exposure number. This stability was considered satisfactory

at the present stage of development of the apparatus but it will be improved by the addition of voltage stabilizers.

Filters

An alcoholic solution of Rhodamine 5 GDN Extra[11] is circulated through a cylindrical filter jacket, and a cooling coil immersed in running tap water. This filter is a modification of the one used by Edsall and Wilson.[1] The p-nitrotoluene of their filter has been replaced by a Wratten 2A gelatin filter which is wrapped around the Polaroids. The gelatin filter is reported[12] to transmit less than 1 percent at 4047, and about 80 percent at 4358.

Polaroid-filter tubes

These tubes consist of successive layers of type H Polaroid,[13] Wratten 2A gelatin filter, and
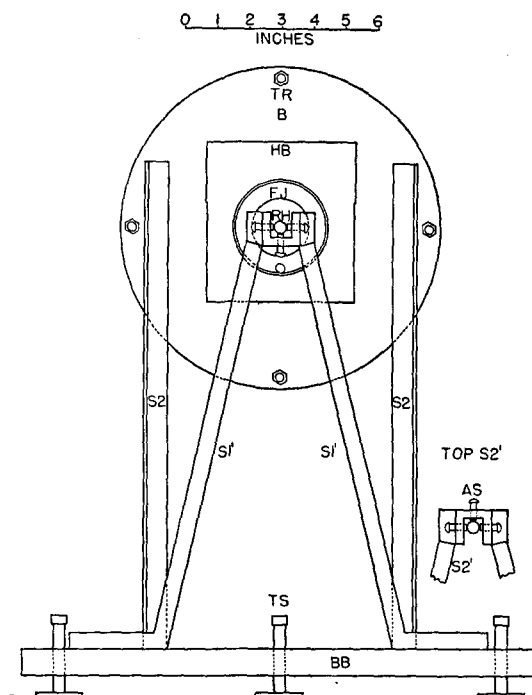
FIG. 2. Rear view of Raman apparatus. Reflector, lamps, and polaroid omitted. See Fig. 1 for legend.

---

[10] The type A-H11, discussed below, give less background and are less sensitive to temperature variations. All the work reported here was done with A-H2 lamps. We are indebted to Dr. Foil A. Miller for suggesting the use of these lamps, and for many other suggestions during the construction of this apparatus.

[11] We are indebted to E. I. duPont deNemours for this dye.
[12] *Wratten Light Filters*, 16th Edition (Eastman Kodak Company, Rochester, New York, 1940).
[13] We are indebted to Mr. C. D. West of the Polaroid Corporation for the Polaroid used. This type H film transmits 34.2 percent of 4358 with a degree of polarization

FIG. 3. Intensity stability of the mercury AH-2 lamps as measured by the Raman line density of successive exposures. *C*, air stream temperature maintained at 80 ±2°C by means of a damper; *U*, air stream temperature uncontrolled.

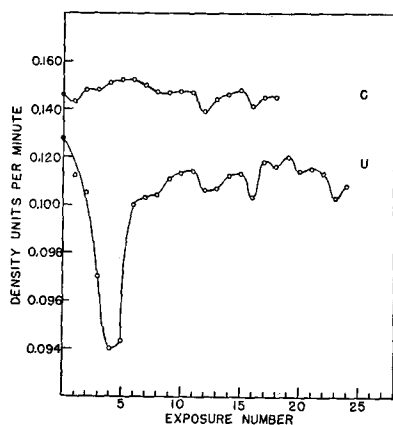protective Cellophane, wrapped around a glass cylinder, and secured with Scotch Tape. Two such cylinders were constructed, identical except that the optical axis of the polaroid on one was perpendicular to the axis of the polaroid on the other. These cylinders are concentric with the Raman tube and are easily changed between exposures from the front of the apparatus.

Raman tubes

The Raman tubes are of conventional Wood design. Each tube is permanently cemented into a brass holder with plaster of Paris; tube and holder are aligned in V-blocks during the cementing. This method allows free interchange of Raman tubes in the illuminator without the necessity of realignment.

Speed

No generally accepted measure of the speed of a Raman apparatus seems to be in use; yet this factor is quite important. We have some work still under way on this matter, and we shall report here that an exposure of about 30 minutes, using the standard conditions described, and a standard plate and development, will bring the 314 cm^{-1} line of CCl$_4$ to a photographic density of 1.0; an exposure of about 13 minutes will bring the 992 cm^{-1} line of C$_6$H$_6$ to this density.

of 0.996, and was used throughout the work reported here. The Polaroid Corporation has since replaced type H with a similar film designated as type K on ABC support.

PHOTOMETRY

Eastman 103a-0 and 103a-J plates, with anti-halation backing, were used throughout this study. They were chosen primarily because of their low reciprocity-law failure; their high speed is also advantageous in Raman work. Plates were developed for two minutes at 17°C in D-8, diluted 1 part of developer to two parts of water; this formula gives less fog than the usual D-19. The resulting gamma is about 2.4.

A series of calibration spectra was impressed upon each plate using a small, coiled-filament bulb operated from a constant-voltage transformer. A blue glass filter and a piece of ground glass were placed in the optical path. Ten calibration exposures were made, using rotating sector disks cut so that the logarithm of the intensity was decreased in steps of 0.2. The calibration exposures were each 2 minutes, compared with Raman exposures on the order of an hour.

We felt that reciprocity-law failure could be ignored for two reasons. First, the plates used were specifically designed to reduce this effect to a minimum. Second, as Reitz[4] pointed out, the time difference between the two spectra will not introduce a serious error since we require relative, and not absolute, data. The desired information is the ratio of the two Raman intensities, and these exposures are of the same duration.

Line densities were obtained with a Leeds & Northrup recording microphotometer and were

TABLE I. Depolarization factors for carbon tetrachloride from individual plates.

Plate No.	Line			
	218	314	459	762–90
H-19	0.86	0.83	0.03	0.80
H-20	0.82	0.78	<0.05	0.88
H-21	0.83	0.85	0.06	0.89
H-22	0.85	0.85	<0.04	0.91
H-23	0.80	0.84	0.03	0.92
H-24	0.78	0.77	0.04	0.88
H-25	0.86	0.82	<0.04	0.81
H-33a	0.88	0.85	<0.08	—
H-33b	0.81	0.80	<0.05	—
H-35a	0.86	0.85	—	—
H-35b	0.83	0.82	—	—
H-35c	0.83	0.82	—	—
H-36	0.78	0.76	0.06	0.93
H-37	0.86	0.90	<0.04	0.85
Average	0.83	0.82	0.04$_4$	0.88
Std. dev.	0.03	0.04	0.01$_4$	0.04
Accepted values	0.857	0.857	0.046	0.857

transformed into relative intensities by means of a characteristic curve constructed from the calibration marks.

The continuous background deserves special attention. Our studies show it to be the greatest single source of error, exceeding even the residual intensity fluctuations of our lamps. Fortunately, the background is polarized and is absent in most of the "parallel" exposures. In cases of relatively strong lines, close together and near the exciting line, background troubles may be complicated by the Eberhard effect.

We used the usual method of correcting for background, transforming background density into intensity from the characteristic curve, and subtracting the result from the line intensity. Strock[14] maintains that even this method provides a spurious, or at best only a partial, correction. He adds, quite correctly, that the only cure for background is to eliminate it. Since we could not achieve this, we determined the proper choice of background on our microphotometer tracings by some studies on carbon tetrachloride. These experiments indicated that, to obtain the accepted values for the carbon tetrachloride lines, the background minimum just in front of the line (i.e., closest to the exciting line; see Fig. 4) should be taken as representing the line background. When this procedure was applied consistently to carbon tetrachloride, the results were acceptable, although slightly low (see Table I). The results could be improved by taking a somewhat higher point as the actual background, but this was not considered advisable since there was no other point on the microphotometer tracing which could be logically and consistently taken as a measure of background. The same choice of background which was worked out for carbon tetrachloride was applied successfully to several other compounds.

We have found that the background can be reduced by using the new General Electric mercury-vapor lamps, type A-H11. These lamps are identical with the type A-H2 except for a reduction in the amount of mercury used. Our preliminary experiments indicate that, for exposures giving equal Raman line densities, the A-H11

[14] L. W. Strock, Proc. 7th Spect. Con. 134 (1940); J. Opt. Soc. Am. **32**, 103 (1942).
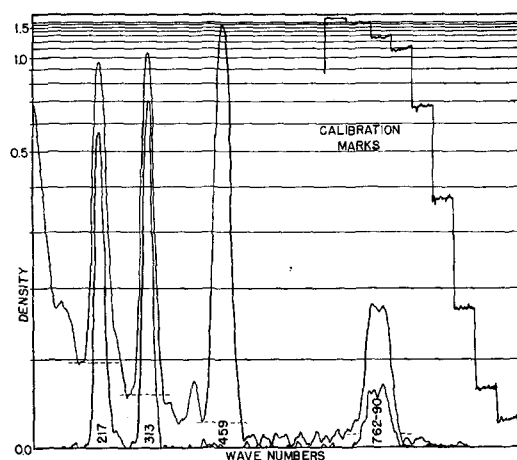

FIG. 4. Microphotometer tracing of the polarized Raman spectra of carbon tetrachloride. The upper tracing is the perpendicular spectrum; the lower is the parallel spectrum. The dashed horizontal lines indicate the background density used for calculating the background correction.

lamps give less than half the background density of the A-H2 lamps. The reduction in background, however, is accomplished at the sacrifice of half of the operating lamp intensity; i.e., the Raman exposures must be twice as long for the same line density. A further reduction in the background could be obtained by running the lamps at a lower operating temperature, but this decreases the lamp intensity still further.

PERFORMANCE

Figure 4 shows a typical tracing of a plate taken to determine the depolarization factors of the stronger lines of carbon tetrachloride. The upper tracing represents the perpendicular spectrum and the lower, the parallel. The calibration marks have been compressed. Particular features to be noted are the complete absence of background in the parallel spectrum, and the complete absence of the parallel component of the 459 line, although the perpendicular component of this line excited by 4348 is plainly visible. (The ratio of the intensities of 4348 to 4358 is about 0.08.)

Table I gives the actual results with carbon tetrachloride for two series of runs. Only one plate was rejected; on this exposure there was an error in the calibration marks caused by slipping of the rotating sectors.

On approximately half the plates, the parallel

TABLE II. The average, average deviation, and maximum deviation of the depolarization factors for the Raman lines of carbon tetrachloride from various sources.

Author	Average depolarization factors				
	Line				
	218	314	459	762	790
Reitz-I (5)†	0.854	0.872	0.045	0.742	0.777
Reitz-II (17)	0.84	0.87	0.04	0.89	0.84
Cleveland (5)	0.853	0.867	0.072	0.847	0.832
This research	0.83	0.82	0.044	0.88	
Theory or accepted	0.857	0.857	0.045	0.857	0.857
Average deviation from the mean					
Reitz-I	0.021	0.030	0.015	0.055	0.028
Reitz-II	0.06	0.07	0.02	0.06	0.08
Cleveland	0.017	0.020	0.057	0.023	0.044
This research	0.03	0.03	0.013	0.03	
Maximum deviation from the mean					
Reitz-I	0.048	0.062	0.027	0.111	0.043
Reitz-II	0.12	0.13	0.05	0.13	0.15
Cleveland	0.035	0.047	0.072	0.036	0.078
This research	0.05	0.08	0.015	0.08	

† Number of observations in parentheses; our calculations are based on the observations recorded in Table I, *viz.*, 14 observations on the 218 and 314 lines, 5 on the 459 line, and 9 on the doublet.

component of 459 was undetectable; in such cases we could only estimate a maximum value of ρ based on the relative intensity of the perpendicular component. Only the five observations which led to a significant result were used in the calculation of the precision measures in Tables I and II. On short-exposure plates, the factor is omitted both for this line and for the doublet. The results on this compound agree with the accepted or theoretical values within the standard deviation.

We present in Table II a comparison of the precision of our results on CCl_4 with that obtained by a few other workers. (Very few investigators report enough data for a precision estimate.) "Reitz-I" refers to his fundamental work,[4a] and "Reitz-II" refers to his control results;[4b] "Cleveland" refers to the paper cited above.[6] The deviations in our data compare

TABLE III. Depolarization factors for chloroform and benzene.

Chloroform			Benzene		
line cm⁻¹	found	accepted††	line cm⁻¹	found	accepted††
262	0.86	6/7	606	0.8	0.81
366	0.18	0.20	849	0.8	0.77
668	0.08	0.06	992	0.04	0.07
760	0.92	0.80	1177	0.8	0.70
1214	0.9	6/7	1585–1606 }	0.9	6/7
3020	0.4	0.31	3046–3063 }	0.3	D 0.4

†† M. Magat, *Tables Annuelles* (Hermann and Cie, Paris, 1937).

favorably even with those of Reitz's fundamental paper.

Additional results on chloroform and benzene are given in Table III. The values for the depolarization factors of benzene are given only to one place since a background correction had to be applied to the parallel spectrum as well as to the perpendicular one. The last two lines of chloroform are reported in the same manner because they were weak.

The advantages of the present apparatus are numerous. Eight high intensity lamps are used, a number impossible with single-exposure methods. The addition of eight more lamps to the present apparatus is contemplated to reduce the already short exposure times. The apparatus is simple, and the optical alignment is not delicate. The polarizing cylinders are easily prepared and are inexpensive. Most important, no "apparatus corrections" are necessary. (The usual photographic-background correction may, of course, cover a multitude of photometric sins.)

The most important disadvantages of this apparatus are not too formidable. The stability of the light source can be improved. The continuous background, which is common to any method, can be reduced by the use of an improved type of lamp.