

## Depolarization Measurements on Raman Lines by an Easy, Accurate Method

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in energy  $(8.3-4.2)=4.1$  kcal. as  $\Delta E$  in the expression  $e^{-\Delta E/RT}$  for the ratio of rates in the two cases of ethane and isobutane.

The activation energy differences here found of 2.8 and 4.1 kcal. between primary and secondary and primary and tertiary reactions compare favorably with the predictions of Rice,<sup>8</sup> 1.2 and 4.0 kcal. based upon the decomposition of hydrocarbon vapors, an analysis of the products and an interpretation of these in terms of assumed activation energies for the various intermediate steps. Our values therefore are contributory evidence in support of the chain mechanism of decomposition of saturated hydrocarbons, and supply reliable data for the activation energies of typical radical-molecule reactions.

We believe that the differences in activation energies here under discussion are closely related to the bond energies in question. We are aware of the dangers attending such an identification of one with the other but we are confirmed in our belief by the data of Kistiakowsky and his

co-workers<sup>9</sup> on the heats of hydrogenation of the substituted ethylenes. Monosubstituted ethylenes on hydrogenation change a double bond to a single C—C bond and form one primary and one secondary C—H bond. With 1,1 disubstituted ethylenes one primary and one tertiary C—H bond are formed. Other types of substitution give other combinations. If the Harvard data be analyzed on this basis, it is found that as many as seven independent thermal measurements for the energy difference, primary-secondary, yield the value  $2.4 \pm 0.25$  kcal. and, for the primary-tertiary difference, three measurements yield 4.4 kcal. We believe this cumulative evidence warrants a confident modification of the first approximation in the estimates of C—H bond energies in hydrocarbons which assigns them all an equal value. We suggest, as a second approximation, bond energy differences of 2.5 and 4 kcal. between primary and secondary and primary and tertiary C—H bonds in saturated hydrocarbons. We are exploring further the consequences of these assumptions.

<sup>8</sup> F. O. and K. K. Rice, *The Aliphatic Free Radicals* (Johns Hopkins Univ. Press, 1935).

<sup>9</sup> G. B. Kistiakowsky *et al.*, J. Am. Chem. Soc. **58**, 137 (1936); **59**, 831 (1937); **60**, 440 (1938).

## Depolarization Measurements on Raman Lines by an Easy, Accurate Method

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The depolarization factors of Raman lines are determined by a method in which a Polaroid disk, so oriented that it passes light whose electric vector is horizontal, is placed between the Raman tube and the lens which condenses the scattered light on the slit of the spectrograph. Two exposures of equal duration are made, one with the arc below, the other with it at the side, of the horizontal Raman tube. The ratio of the intensities in the two exposures (depolarization factor) is determined by comparison with the lines of seven argon spectra produced by argon light of known intensity ratios. Important advantages of the method are the comparatively short exposure times and the elimination of errors due to the polarization characteristics of the spectrograph. Results for the depolarization factors of Raman lines obtained from a mixture of benzene and carbon tetrachloride are given and comparison with previous data for these compounds is made.

**A**LTHOUGH information regarding the depolarization factors of Raman lines is of the greatest importance in assigning the frequencies

to particular modes of vibration within the molecule, comparatively few data have been reported because of the difficulty and expense

connected with the methods previously used. Recently Edsall and Wilson<sup>1</sup> have described two arrangements which represent significant steps in the direction of making such measurements more universal in the Raman spectra field.

#### DISCUSSION OF THE EDSALL-WILSON ARRANGEMENTS

In the first of these, light from four vertical mercury lamps, backed by parabolic reflectors, was passed through a cylinder of Polaroid so oriented that it transmitted light whose electric vector was parallel to the axis of the vertical Raman tube. A second exposure was made without the Polaroid and with the intensity of illumination reduced to the extent necessary to give the depolarized lines equal intensities in the two exposures. Lines which had nearly the same intensity in the two exposures were designated by *D* (depolarized) while lines whose intensities were appreciably different were designated by *P* (polarized). The method is an ingenious one for the qualitative distinction between polarized and depolarized lines, which is the purpose the authors had in mind. However, the considerations given below indicate that, from a quantitative point of view, the values of the *depolarization factors* (subsequently referred to as  $\rho$ ) obtained by such a method would be too large.

Consider a *completely* polarized line: During the first exposure the electric vector is parallel to the axis of the Raman tube, hence no light will be scattered along the axis of the tube. In the second exposure, since polarized light is not employed, there will be components of the electric vector both perpendicular and parallel to the axis of the Raman tube. The component parallel to the axis will, as before, result in no scattering, but the perpendicular component will give scattering along the axis. Dividing the intensity of the line in the first exposure by its intensity in the second exposure, one obtains a value of zero for  $\rho$ , as is to be expected.

If, however, the line is partially depolarized, as practically all Raman lines are, it appears that an erroneous value of  $\rho$  would result. For, in reducing the intensity of all the lines on the plate

to make the highly depolarized lines have the same intensity in the two exposures, the denominators of the depolarization ratios are made too small and consequently the values of  $\rho$  will be too large for all the lines on the plate. The only exception is the *completely* polarized line discussed above.

These points may be clarified by a consideration of Table I. Imagine three Raman lines, each with an intensity of 10, and having values of  $\rho$  equal to 0.86, 0.50 and 0.02, respectively. The upper part of the table gives the relative intensities that would have been obtained if the incident radiation had been polarized. The lower part of the table gives the relative intensities that would be obtained by the method of Edsall and Wilson, the corresponding values of  $\rho$ , and the errors in  $\rho$ .

For determining quantitative values of  $\rho$ , the method would be more exact if the intensity of the highly depolarized line in the second exposure had been made 7/6 as strong as in the first exposure. This would increase the intensities of the other two hypothetical lines by the same amount and the apparent values for  $\rho$  (Cf.

TABLE I. Comparison of the values of  $\rho$  for three hypothetical Raman lines of equal intensity obtained by use of polarized light and by the method of Edsall and Wilson.

METHOD	INCIDENT LIGHT	INTENSITY OF:		
		HIGHLY DEPOLARIZED LINE	PARTIALLY DEPOLARIZED LINE	HIGHLY POLARIZED LINE
Polarized incident light	Electric vector parallel to axis of Raman tube	4.6	3.3	0.2
	Electric vector perpendicular to axis of Raman tube	5.4	6.6	9.8
	True values of $\rho$	0.86	0.50	0.02
Edsall and Wilson	Electric vector parallel to axis of Raman tube	4.6	3.3	0.2
	Not polarized and intensity reduced	4.6	4.6	4.6
	Apparent values of $\rho$ Errors in $\rho$ values	1.00 0.14	0.72 0.22	0.04 0.02

<sup>1</sup> J. T. Edsall and E. B. Wilson, Jr., J. Chem. Phys. 6, 124-127 (1938).

Table I) would then be 0.86, 0.61 and 0.04 with corresponding errors of 0.00, 0.11 and 0.02, rather than 0.14, 0.22 and 0.02, as before.

Another possibility would be to adjust the intensity so that the  $\rho$  value of some other line, e.g. one for which  $\rho = 0.5$ , was correct. The result of this procedure, however, would be to make the  $\rho$  values for the highly depolarized lines too small.

Thus, in view of the foregoing discussion, it must be concluded that, as long as polarized light is used during one exposure and unpolarized light during the other, it is impossible to obtain quantitative values of  $\rho$ .

From the quantitative point of view, the arrangement would be vastly improved if during the second exposure a cylinder of Polaroid, constructed in such a manner that it transmitted only light whose electric vector was perpendicular to the axis of the Raman tube, had been employed. This would eliminate the troublesome parallel component and would also make the absorption of light by the Polaroid the same in the two exposures.

In the second arrangement used by Edsall and Wilson, light from a mercury arc was passed through a filter solution contained in a cylindrical glass tube which concentrated the light in a nearly parallel beam, through a plane sheet of Polaroid, along the axis of the Raman tube. Two exposures of equal duration were made, one with the Polaroid in a position to transmit light whose electric vector was parallel to the axis of the Raman tube, the second with the Polaroid rotated through an angle of  $90^\circ$ . Again, the intensity of illumination was reduced during the second exposure to make the strongly depolarized lines have the same intensity as in the first exposure. This arrangement would be satisfactory for quantitative purposes if the intensity during the second exposure were not reduced and if some method of correcting for the polarization characteristics of the spectrograph were employed. A major disadvantage, however, is that exposure times of the order of 24 hours were required for each of the two exposures, even with a fast spectrograph of aperture ratio  $f : 3$ .

The present authors began preliminary experiments<sup>2</sup> with the use of Polaroid in November

TABLE II. Comparison of intensities of three hypothetical Raman lines with mercury arc and Polaroid in various positions.

	MER- CURY ARC	POLAROID SET SO THAT TRANSMITTED ELECTRIC VECTOR IS:	INTENSITY OF:		
			HIGHLY DEPO- LARIZED LINE	PAR- TIAL- LY DEPO- LARIZED LINE	HIGHLY PO- LARIZED LINE
A	Side	Horizontal	4.4	3.3	0.2
		Vertical	5.6	6.6	9.8
B	Below	Vertical	4.4	3.3	0.2
		Horizontal	5.6	6.6	9.8
C	Side Below	Horizontal	4.4	3.3	0.2
		Horizontal	5.6	6.6	9.8

1937, but were able to make only qualitative measurements at that time. Experimentation was resumed a year later and a method, similar in some respects to the second arrangement of Edsall and Wilson, has been developed. This method permits quantitative values of  $\rho$  to be determined with relatively short exposure times and with elimination of errors due to selective reflection of the polarized light in the spectrograph.

#### EXPERIMENTAL PROCEDURE

Light from a cylindrical mercury vapor lamp<sup>3</sup> is passed through a test tube (21 mm in diameter) which contains the excellent filter solution used by Edsall and Wilson, and is concentrated in a nearly parallel beam along the axis of the horizontal Raman tube. The distance from the center of the filter tube to the center of the Raman tube is 25 mm and is kept constant by collars of wood which slip over the tubes. The mercury arc is adjusted so that the distance from its center to the center of the filter tube is 25 mm. Accuracy of adjustment is tested by holding a piece of thin white cardboard at the edge of the Raman tube opposite the light source. When the mercury arc, filter tube, and Raman tube are properly aligned, a symmetrical light strip, bordered by dark lines, appears on the cardboard. The cardboard is then replaced by a plane mirror in order to reflect the incident beam back upon itself and thus to increase the intensity of illumination.

<sup>2</sup> Forrest F. Cleveland and M. J. Murray, Phys. Rev. **53**, 330 (1938).

<sup>3</sup> Forrest F. Cleveland and M. J. Murray, Am. Phys. Teacher **5**, 270-272 (1937).

The scattered light is intercepted approximately 30 cm in front of the Raman tube by a Polaroid disk so oriented that it passes that component of the light whose electric vector is horizontal. Two exposures of equal duration are made, one with the mercury arc below, the other with it at the side, of the Raman tube. The current through the arc is carefully maintained at a constant value during the two exposures. The width of the slit is set at 0.17 mm. The film used was Agfa Super Plenachrome Press.

The method used for comparing the intensities of a given line in the two exposures is as follows: Seven argon spectra are photographed upon the same film with the intensities of the incident light varying in the ratios of 7 : 6 : 5 : 4 : 3 : 2 : 1, the exposure time for each being three hours, the same as that for the polarization film above. This variation in intensity is obtained by adjusting the perpendicular distance of an argon lamp (2 w, 110 v, a.c.) from a plane of white cardboard, placed in front of the one-hole stopper which normally holds one end of the Raman tube.

The stronger of the pair of lines on the polarization film is now matched with one of the lines in the same wave-length region on the most intense argon spectrum. The weaker of the Raman pair is then matched with the *same* argon line on one of the less intense argon spectra. The value of  $\rho$  is then given by the ratio of the two intensities. Thus, if the weaker of the Raman pair matches the line on the least intense argon spectrum, the value of  $\rho$  would be 1/7. If it matches the line on the next to the strongest argon spectrum,  $\rho$  would be 6/7, the theoretical maximum.

#### DISCUSSION OF METHOD

The ratio of the intensity of the Raman line in the second exposure (arc at the side) to that in the first exposure (arc below) gives the depolarization factor of the line. This may be made clear by reference to Table II. Imagine three lines, each of intensity 10, having  $\rho$  values of 0.86, 0.50 and 0.02, respectively. If the measurement were made by one of the standard methods,<sup>4</sup> in which the Polaroid is placed between the Raman tube

and the lens which condenses the scattered light on the slit of the spectrograph and in which the Polaroid is rotated through an angle of 90° between the two exposures, the relative intensities would be those given in part *A* and part *B* of Table II, depending upon the position of the mercury arc. This, of course, assumes that correction has been made for the selective reflection of the polarized beams at the prisms of the spectrograph. Comparing these intensities with those obtained by the present method, part *C*, one finds that the same values of  $\rho$  would be obtained as in the standard method. *The present method, however, has the great advantage that, since the Polaroid remains fixed, there is no error caused by the polarization characteristics of the spectrograph.*<sup>5</sup>

Placing the Polaroid between the Raman tube and the spectrograph reduces the exposure time because it eliminates the strong absorption of the blue exciting light (Hg 4358Å) before it reaches the Raman tube. The Raman lines (exclusive of the anti-Stokes lines) have longer wave-lengths and are not absorbed as greatly as the exciting light. While a Raman line of low displacement suffers a greater absorption in passing through the Polaroid than one of high displacement, this introduces no error into the results since only intensities of lines having the same displacement are compared in determining the values of  $\rho$ . The percentage of absorption of a given Raman line will be the same in the two exposures.

The use of a rather large slit width is made possible by the very complete absorption of the continuous mercury radiation by the filter solution employed.<sup>1</sup> The loss in resolution is more than compensated by the reduction in exposure time thus made possible.

Since the ratio of the densities of the lines on the polarization film is not the same as the ratio of the intensities of the light that produced them (unless the intensities happen to be identical), it was necessary to devise a method whereby the true intensity ratios could be obtained. In the method described above, the ratio of the intensity of the light which produced a given argon line in one of the weaker spectra to that of the light

<sup>4</sup> K. W. F. Kohlrausch, *Der Smekal-Raman-Effekt* (Julius Springer, Berlin, 1931), p. 108.

<sup>5</sup> Cf. K. W. F. Kohlrausch, *Der Smekal-Raman-Effekt, Ergänzungsband* (Julius Springer, Berlin, 1938), p. 84.

TABLE III. Depolarization factors of the Raman lines of  $\text{CCl}_4$ .

$\Delta\nu^*$ ( $\text{cm}^{-1}$ )	$I^*$	CARRELLI- PRING- SHEIM- ROSEN†	CABANNES†	BHAGA- VANTAM†	OUR RE- SULTS	TABLES AN- NUELLES*
218	7	0.8	—	0.75	6/7	~6/7
314	8	0.9	—	0.8	6/7	~6/7
459	10	0.05	0.05	0.1	0.1	0.046
762	2	0.7	—	0.75	0.8	0.79
790	2	—	—	0.75	0.8	0.78
1535	0	—	—	0.33	—	0.3

\* M. Magat, *Tables Annuelles* (Hermann & C<sup>ie</sup>, Paris, 1937), p. 26.  
† Reference 4, p. 111.

which produced the same line in the strongest spectrum is accurately known. Consequently, if the Raman pair on the polarization film matches these argon lines in density, it is evident that the ratios of the intensities of the Raman lines must be the same as that of the argon lines. Other conditions such as temperature, nature of the film, time of exposure, and wave-length region used in matching, must, of course, be held constant. One has in this method of comparing the intensities an absolute method which depends in no way upon any assumption as to the relation between the density of the line and the intensity of the incident light.

A most useful technique is that of adding a relatively small amount of  $\text{CCl}_4$  to the liquid. One can then determine by rapid inspection whether there is any departure from the proper intensity in the two exposures by checking the depolarization factors of the strong  $\text{CCl}_4$  lines against the accepted values. The percent of  $\text{CCl}_4$  added should be small when the exposure time is great in order that its spectrum may not be so strong as to preclude accurate comparison of the intensities.

The present method is believed to be sufficiently easy in operation and accurate in its results to warrant the hope that future investigators may report depolarization factors for all the principal lines of the compounds which they study.

#### CHARACTERISTICS OF SPECTROGRAPH

The spectrograph was constructed from optical parts having the following characteristics: *Slit*: symmetrical slit, Gaertner L162-b; *collimating lens*: focal length 490 mm, aperture 52 mm; *two prisms*: glass, 60°,  $n_d$  1.65, height 45 mm, base

TABLE IV. Depolarization factors of the Raman lines of  $\text{C}_6\text{H}_6$ .

$\Delta\nu^*$ ( $\text{cm}^{-1}$ )	$I^*$	DAURE†	CARRELLI- PRING- SHEIM- ROSEN†	CA- BA- NNES†	BHAGA- VANTAM†	OUR RE- SULTS	TABLES ANNU- ELLES*
606	5	—	1	~1	1	0.8	0.81
849	2	—	1	—	1	~6/7	0.77
992	10	<0.2	0.7	0.04	<0.05	0.1	0.07
1177	2	—	1	~1	—	0.8	0.70
1480	0	—	—	—	—	—	D
1585	3	—	1	~1	1	0.8	~6/7
1606	2	—	—	—	—	—	~6/7
2949	5	—	—	—	—	6/7	—
3046	4	—	—	—	—	—	D
3063	8	>0.5	0.7	0.6	1 0.35	0.3	0.4
3187	1	—	—	—	—	—	P

\* M. Magat, *Tables Annuelles* (Hermann & C<sup>ie</sup>, Paris, 1937), p. 75-76.  
† Reference 4, p. 111.

75 mm; camera lens: focal length 400 mm, aperture 50 mm. The linear dispersion of the spectrograph is approximately 33A/mm at 4500A.

#### EXPERIMENTAL RESULTS

In order to test the method, the depolarization factors of the Raman lines of  $\text{CCl}_4$  and  $\text{C}_6\text{H}_6$ , were determined from the spectra of a mixture containing approximately 15 percent  $\text{CCl}_4$ . Comparison of the values obtained with those of other workers is made in Tables III and IV. The exposure time was three hours for each position of the arc. Longer exposures would be necessary to obtain data for the weaker lines. The use of a comparatively wide slit prevented the resolution of the doublets 1585, 1606 and 3046, 3063. The use of a narrower slit and longer exposure times would be necessary to resolve these doublets.

The depolarization factors of a series of derivatives of phenylacetylene are being determined by this method. It has been found that three-fourths of an hour for each exposure is sufficient to give adequate density for the principal lines of these compounds.

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