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A Simple Method for Determining the Polarization of Raman Lines

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A simple method is described for determining qualitatively the polarization of Raman lines. The incident light is polarized by means of "Polaroid." One of the arrangements used permits very high intensity of incident illumination. A brief statement of the theory of the method is given, and experimental data on acetic acid, acetone and ethanol are presented.

THE determination of the polarization of Raman lines is of great importance in assigning these lines to modes of molecular vibration. The usual methods of measuring this polarization are, however, rather difficult and involve the use of expensive apparatus, so that relatively few such measurements have been reported. Ordinarily, unpolarized incident light is used, and the scattered radiation is resolved into two components by a birefringent prism. Now that large sheets of transparent polarizing material ("Polaroid") are available at relatively low cost, we have found it possible to determine qualitatively the polarization of Raman lines with considerable ease. When the spectra are photographed in a suitable manner, it is possible to discriminate sharply between polarized and depolarized frequencies.

EXPERIMENTAL PROCEDURE

Two different experimental arrangements have been used. In one, the cell containing the liquid is illuminated by four vertical mercury lamps¹ equipped with parabolic reflectors. See Fig. 1. A cylinder of Polaroid,² made so that it transmits only light polarized with its electric vector parallel to the axis of the cylinder, slips over the Raman tube. Two exposures are made: one with all the lamps operating and the Polaroid in place, and the other with reduced illumination and with no Polaroid. It is necessary to reduce the illumination for the second exposure in order to obtain two pictures of comparable intensity

¹ The lamps, Raman cell, and several other parts were made by Professor G. B. Kistiakowsky and we are deeply indebted to him for his kindness in placing them at our disposal.

² We are indebted to the Polaroid Corporation for supplying us with this cylinder.

inasmuch as Polaroid absorbs rather strongly the violet light used in these experiments. As will be shown later, all Raman lines arising from unsymmetrical vibrations of the molecule should show the same decrease in intensity when the Polaroid is used, whereas lines associated with completely symmetrical vibrations will usually be attenuated more strongly. Consequently, the most sensitive way to distinguish the symmetrical vibration frequencies is to adjust the light intensity of the second exposure so that all the depolarized lines (unsymmetrical vibrations) have equal intensities on the two plates. The polarized lines should then stand out because of their unequal intensities. Because of the failure of the photographic reciprocity law, it is safest to use the same exposure time for the two pictures, but different intensities of illumination.

We have also made use of a second method, which has the advantage of great simplicity, although the light intensity is relatively low, and long exposures are therefore required. This is based on the experimental arrangement devised by Wood³ and is shown diagrammatically in Fig. 2, which represents a cross section perpendicular to the axis of the Raman tube. The light from a single mercury arc (*A*) passes through the cylindrical tube *F*, which contains a solution which acts as a light filter, and also as a lens, gathering the light from the arc into a concentrated and nearly parallel beam. This light then passes through the plane Polaroid disk (*P*), which can be so oriented as to transmit light which vibrates either parallel or perpendicular to the axis of the Raman tube (*R*). An exposure is first taken with the plane of the

³ R. W. Wood, *Physical Optics*, third edition, 1934, Chapter XIV.

incident light parallel to the axis of *R* (perpendicular to the plane of the paper); then the Polaroid disk is revolved through a right angle (around the axis indicated by the arrow in Fig. 2) to admit light polarized perpendicular to the plane of the paper, and a second exposure is given for an equal time.

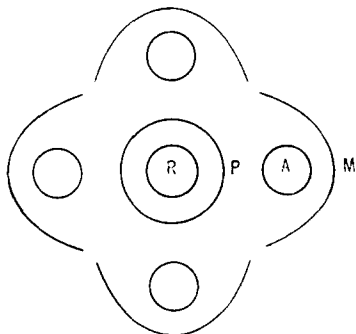


FIG. 1. Diagram of one type of apparatus used (top view). *R* is Raman tube in cross section; *P*, Polaroid cylinder; *A*, mercury arc; *M*, parabolic reflector.

As with the first method, it is very desirable to adjust the light intensity in the second exposure so that depolarized lines have the same intensity in both exposures. It was found that three plane thin glass sheets⁴ placed between the Polaroid disk and the Raman tube during the second exposure accomplished this result quite satisfactorily. (See the photographs reproduced below.) These results were obtained with a Hilger E-439 glass spectrograph; the exact intensity ratio for the two polarized beams will vary somewhat from one spectrograph to another, depending on the degree to which polarized light is reflected from the prisms of the spectrograph.

It is essential, of course, in photographing these spectra, that the axes of the mercury arc, the Raman tube, and the collimator of the spectrograph should all be parallel and in the same plane; also the plane of polarization of the light transmitted by the Polaroid must be carefully adjusted.

Filters

Either of the methods described requires two separate exposures. The intensity of the highly polarized Rayleigh scattering (including the continuous background) will be very much greater

⁴ Microscope slides were found very convenient for this purpose.

in one exposure than in the other. It is desirable, therefore, to reduce the continuous background as nearly as possible to zero in *both* exposures. A filter which nearly achieves this purpose has been devised by Sannié, Amy and Poremsky,⁵ and we have used a slight modification of the filter which they recommend. This consists of an alcoholic solution of *p*-nitrotoluene and rhodamine 5GDN Extra.⁶ A solution of 2 percent *p*-nitrotoluene, and one part in 50,000 of the rhodamine dye, in a layer 30 mm thick, completely absorbs the ultraviolet, transmits less than 1 percent of $\lambda 4047$ and about 1 percent of $\lambda 4916$, while transmitting 70 percent or more of $\lambda 4358$. Transmission falls rapidly on either side of $\lambda 4358$, so that the continuous background between 4500 and 5000Å is very largely wiped out; furthermore, Raman lines are excited by the 4358 triplet and by this alone,⁷ so that there is no difficulty in the assignment of frequencies.

Long exposures are required by the second method here described. We have found it most satisfactory to give 24 hours for each of the two exposures in order to obtain the fainter Raman lines in such substances as acetic acid or ethanol.⁸

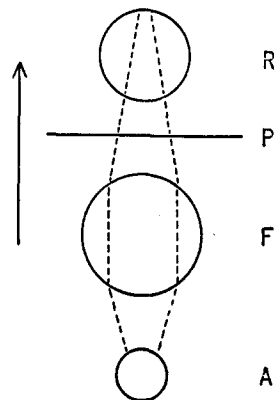


FIG. 2. Diagram of second type of apparatus. *R*, Raman tube; *P*, Polaroid disk, *F*, filter tube; *A*, mercury arc.

⁵ C. Sannié, L. Amy and V. Poremsky, *Bull. Soc. Chim. France* 3, 2018 (1936). These authors used nitrobenzene and rhodamine 5G Extra, dissolved in alcohol. We have not been able to obtain the latter dye, but rhodamine 5GDN Extra appears to give essentially identical results.

⁶ This dye was supplied to us through the courtesy of E. I. duPont de Nemours and Co.

⁷ The filter completely absorbs the green region of the spectrum, but freely transmits the yellow mercury lines. The presence of the latter, of course, does no harm; in fact it facilitates the focusing of the light from the Raman tube upon the spectrograph.

⁸ Substances like carbon tetrachloride, which yield only a few, very intense Raman lines, can be photographed in a very much shorter period.

This is true even with the use of the Hilger E-439 spectrograph (aperture ratio $f:3$). With spectrographs of low light-gathering power, the time involved would be prohibitively long, and only the first method would be worth considering.

A word may be added regarding the advantages and disadvantages of Polaroid, as compared with other polarizers, such as birefringent prisms. The advantages are several: (1) Very high incident illumination may be used, if the first method described here is employed. (2) The technique is relatively simple. (3) The materials are inexpensive. On the other hand, there are two important disadvantages: (1) Polaroid absorbs strongly in the blue-violet region: a nonabsorbing polarizer would probably transmit three or four times as much light of these wavelengths. (2) It is necessary to make two separate exposures in employing either of the techniques described.

THEORETICAL CONSIDERATIONS

Placzek⁹ has shown that for polarized incident light, the radiation scattered in the direction parallel to the electric vector of the incident light has the intensity

$$I_{||} = 6\gamma^2_{VV'} kI, \quad (1)$$

for a given vibrational transition VV' . Here k is a constant, I is the intensity of the incident polarized illumination, and $\gamma^2_{VV'}$ is the matrix element between the vibrational states V and V' of the quantity

$$\gamma^2 = \frac{1}{2} \{ (C_1 - C_2)^2 + (C_2 - C_3)^2 + (C_3 - C_1)^2 \}, \quad (2)$$

in which C_1, C_2, C_3 are the principal values of the polarizability tensor of the scattering molecule. The light which is scattered in a direction perpendicular to the direction of the electric vector of the incident illumination has the intensity

$$I_{\perp} = (5A^2_{VV'} + 7\gamma^2_{VV'}) kI, \quad (3)$$

in which $A^2_{VV'}$ is the matrix element of

$$A^2 = (C_1 + C_2 + C_3)^2. \quad (4)$$

In the experimental arrangement shown in

Fig. 2, the incident light is polarized first parallel to the axis of the Raman tube and secondly perpendicular to that axis. In the first case, Eq. (1) applies; in the second, Eq. (3). The ratio of intensities is

$$I_{||}/I_{\perp} = \frac{6\gamma^2_{VV'}}{5A^2_{VV'} + 7\gamma^2_{VV'}}, \quad (5)$$

Vibrational transitions can be divided into two classes, those for which $A^2_{VV'} = 0$ and those for which $A^2_{VV'} \neq 0$. All fundamentals involving unsymmetrical vibrations belong to the former class; consequently $I_{||}/I_{\perp} = 6/7$ for such frequencies when the experimental arrangement of Fig. 2 is used. The symmetrical frequencies may have ratios anywhere between zero and 6/7.

If the illumination comes from all sides as in Fig. 1, exactly the same result is obtained as in Eq. (5). This follows from the theorem that no matter what the distribution of light as a function of angle about the axis of the Raman tube,¹⁰ the equation $I_x + I_y = I_z$ holds, where I_x, I_y and I_z are the intensities of the light polarized in the two directions perpendicular and the direction parallel to the axis of the Raman tube, respectively. This theorem can be proved as follows. Let $I(\varphi)d\varphi$ be the total intensity falling radially on the Raman tube from an angular wedge $d\varphi$. Then the contributions of this intensity to I_x, I_y and I_z are $\frac{1}{2}I(\varphi)\cos^2\varphi d\varphi$, $\frac{1}{2}I(\varphi)\sin^2\varphi d\varphi$, $\frac{1}{2}I(\varphi)d\varphi$, respectively. Integration over φ gives

$$I_z = \frac{1}{2} \int_0^{2\pi} I(\varphi) d\varphi = \frac{1}{2} \int_0^{2\pi} I(\varphi) \sin^2 \varphi d\varphi + \frac{1}{2} \int_0^{2\pi} I(\varphi) \cos^2 \varphi d\varphi = I_x + I_y. \quad (6)$$

Consequently if two cylinders of Polaroid are used, one transmitting I_z only, the other light tangentially polarized, Eq. (5) can be used.

It is possible to replace the exposure with illumination polarized perpendicularly (I_{\perp}) by one using unpolarized light. The expression for the ratio of the intensities of the two exposures then becomes

¹⁰ The light is assumed to strike the Raman tube radially. In practice, baffles may be needed to prevent light from falling on the tube nonperpendicularly.

⁹ G. Placzek, Marx, *Handbuch der Radiologie*, Vol. VI.

$$\frac{\text{Polarized } \parallel}{\text{Unpolarized}} = \frac{6\gamma^2_{VV'}}{5A^2_{VV'} + 13\gamma^2_{VV'}} \quad (7)$$

This is the method actually used with the apparatus shown in Fig. 1.

EXPERIMENTAL RESULTS

Polarization photographs of acetic acid, acetone and ethanol are shown in Figs. 3, 4 and 5 (obtained by the second method). Note that the only mercury lines appearing in these photographs are those of the 4358A triplet; all other lines are Raman lines. The data are listed in Table I, where numbers in the top row give

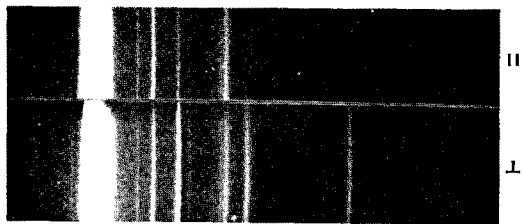


FIG. 3. Acetic acid.

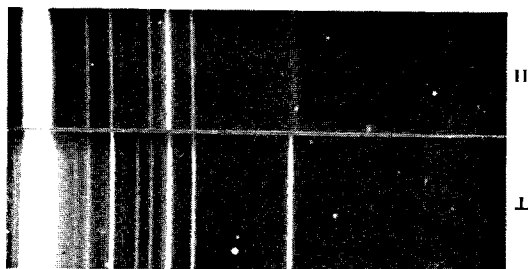


FIG. 4. Acetone.

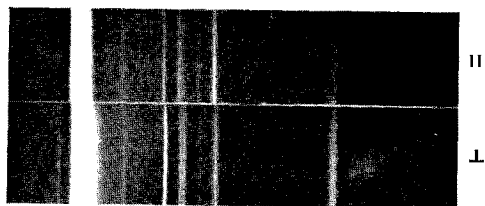


FIG 5 ETHANOL.

TABLE I.

Acetic Acid					
446 (1) <i>(0.59)</i> <i>D</i> ?	621 (3) <i>0.89</i> <i>D</i>	893 (5) <i>0.16</i> <i>P</i>	1024 (1) <i>—</i> <i>D</i> ?	1221 (1) <i>—</i> <i>—</i>	
1277 (1) <i>—</i> <i>—</i>	1366 (2) <i>0.21</i> <i>P</i>	1431 (3 <i>b</i>) <i>0.85</i> <i>D</i>	1663 (2 <i>b</i>) <i>0.37</i> <i>P</i>	2940 (8) <i>0.04</i> <i>P</i>	
Acetone					
391 (1) <i>0.87</i> <i>D</i>	532 (3 <i>b</i>) <i>0.70</i> <i>D</i>	788 (8) <i>0.20</i> <i>P</i>	1067 (2) <i>0.64</i> <i>P</i>	1122 (2) <i>0.88</i> <i>D</i>	1350 ($\frac{1}{2}$) <i>0.23</i> <i>—</i>
1708 (5 <i>b</i>) <i>0.38</i> <i>P</i>	2838 (1) <i>—</i> <i>—</i>	2922 (12 <i>b</i>) <i>0.22</i> <i>P</i>	2965 (4 <i>b</i>) <i>—</i> <i>—</i>	3005 (4 <i>b</i>) <i>—</i> <i>—</i>	
Ethanol					
432 (6) <i>0.55</i> <i>P</i>	884 (60) <i>0.31</i> <i>P</i>	1051 (32) <i>0.59</i> <i>P</i>	1095 <i>—</i> <i>P</i>	1274 (17) <i>—</i> <i>D</i> ?	1455 (46) <i>0.90</i> <i>D</i>
2878 (58) <i>0.14</i> <i>P</i>	2928 (100) <i>0.23</i> <i>P</i>		2972 (61) <i>0.87</i> <i>D</i>		3359 (107 <i>b</i>) <i>—</i> ?

frequency and estimated intensity of each line,¹¹ the second row gives the value measured by Simons for the depolarization ratio, and the third row indicates whether the line is polarized (*P*) or depolarized (*D*) according to our own measurements. In general there is very good agreement between the two estimates. The line at 1095 in ethanol (on which Simons did not report) is found to be strongly polarized, much more so than the line at 1051. We also find (in agreement with Simons) that the line at 1067 in acetone is strongly polarized, contrary to the suggestion of Kohlrausch and Pongratz¹² that it might be depolarized.

Previous measurements, employing the present technique (method 2), have already been reported by one of us.¹³

¹¹ Values taken from Landolt-Börnstein, *Tabellen*, fifth edition, 3d Ergänzungsband, Part II. The polarization measurements (by Simons) are taken from the same source.

¹² K. W. F. Kohlrausch and A. Pongratz, *Zeits. f. physik. Chemie* **27B**, 176 (1934).

¹³ J. T. Edsall, *J. Chem. Phys.* **5**, 225, 508 (1937).