METHODS OF MEASURING LINE INTENSITY IN RAMAN SPECTRA

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AT the present time Raman optical spectra are used in many fields of science and engineering. In using these spectra, investigators are making more and more use of line intensities in addition to wavelengths. Quantitative molecular spectral analysis by Raman spectra is based on the measurement of line intensities. The intensity of a Raman line serves as an important source of information on the structure of molecules and makes it possible to establish the presence of a number of unique structural groups which have certain definite characteristics. In a number of cases "anomalous" values of the intensities of Raman lines indicate definite structural features of a molecule (for example, conjugation shortening of bonds). Hence, the acquisition of reliable data expressed on a standardized intensity scale for various materials is of great value. Furthermore, in recent years a number of investigators have been concerned with the theory of the electrical-optical parameters in Raman spectra—the intensity and depolarization. In order to compare the theoretical results with experimental data it is obviously necessary to have precise methods for measuring these parameters. The data of different authors indicate considerable discrepancies even in cases in which the quantities can be measured fairly easily.

Since precise methods of measuring and analyzing experimental data are now available and allow us to obtain unique and reproducible values for the intensities of Raman lines, we feel it desirable to make a short survey of these methods. A survey of this kind is all the more necessary since experimental techniques in this field have become so diversified. The experimenter now has at his disposal high-dispersion spectrographs with photoelectric detection as well as new light sources— low-pressure mercury tubes. In order to make best use of these new instruments it is useful for us to make a comprehensive analysis of all the factors which are of importance in measuring line parameters in the Raman spectra.

The first questions which arise are which quantities should be measured and how the measurements should be carried out so that the results be uniquely characteristic of the material being investigated. The answer to this problem has several aspects, depending on the instrument which is used and on the method by which the spectrum is recorded.

The experimental investigation of Raman spectra involves certain difficulties which are relatively rare in the study of emission spectra. These difficulties arise because Raman lines are very weak and, as a rule, are usually superimposed on a continuous background, the intensity of which is sizable compared with the Raman lines themselves. The second feature of Raman lines is the fact that these lines have a considerable natural width; even for a narrow line this width is several times greater than the "normal" slit width in the apparatus which is generally used. Since the widths of Raman lines vary over wide limits (a factor of 10 to 20), in measuring line peaks it is difficult to set up conditions for which one quantity has a unique physical significance, i.e., the intensity at the maximum I_0 or the integrated intensity I_∞. The measured intensity of a Raman line is affected by the width and shape of the exciting line, the depolarization of the line, the temperature of the sample, and the characteristics of the apparatus which is used; these factors must be taken into account in obtaining reliable results. It should be recalled, finally, that the entire Raman spectrum lies in a rather narrow spectral range, approximately 300 A (the most intense part of the spectrum lies between 0 and 1600 cm^{-1}), so that many lines overlap.

Although the general principles of measuring the parameters of spectral lines are the same in both cases, the difficulties indicated above make it impossible to use the methods used for emission spectra in studying Raman spectra.

The quantity which most directly characterizes intensity and which is comparatively easily measured is the intensity at the line peak. Generally, however, this quantity does not have a unique physical significance. Depending on the conditions of measurement, the intensity of the peak of the line may be proportional to the intensity at the line maximum I_0, the integrated intensity I_∞, or some intermediate value. Hence, in order to obtain the quantities I_0 or I_∞ by measurements of the intensities at the line peak, it is necessary to take

FIG. 1. Shapes of reference lines used for characteristics: 1) dispersion shape $p/q = \infty$, $r = 1$; 2) Gaussian shape, $p/q = 0$, $r = 1.47$; 3) Voigt shape, $p/q = 0.6$, $r = 1.208$.
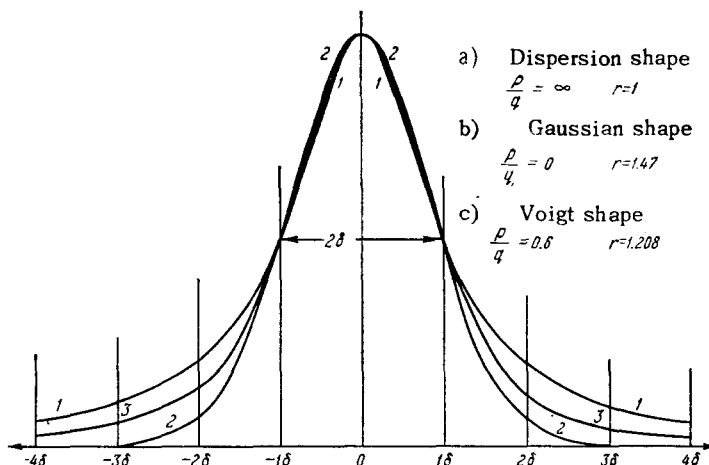
account of the width of the lines being investigated and any distortion effects which may be introduced by the apparatus being used. In a number of cases it turns out to be more convenient to carry out this measurement under "intermediate" conditions when the direct measurements of the intensities at the peaks are not reliable. By calibrating the apparatus it is possible to relate these provisional intensities to the quantities I_0 or I_∞; however, it is necessary to estimate the width of the lines being investigated in order to carry out this procedure. In this method it is of great value to make the measurements under standard conditions. In practice this method turns out to be completely applicable for a number of problems, including molecular spectral analysis. A detailed description of these methods is given in our monograph[1] and no details are given here. We may note however that no severe requirements are imposed on the dispersion and resolving power of the spectrograph.

More detailed information about a line can be obtained by working with a spectrograph with high dispersion and resolving power; instruments of this type are the DFS-4 and DFS-12 spectrophotometers. Because photoelectric detection is used in these instruments it is possible to make direct measurements of the line shapes in Raman spectra. In principle, it is possible to eliminate completely the distorting effects of the spectrograph and the exciting line and to obtain the true shapes of the Raman lines (see reference 2). This type of investigation has been described in detail in reference 3, so that here we give only a brief description of the general method.

We start with an analysis of the observed shapes of Raman lines and exciting lines without working preliminary assumptions as to the true shape of these lines and the apparatus function. It is first necessary to determine which quantities charac-

terize the lines as observed. The quantities that characterize most directly the spectral lines and which are easily measured are:

1) the intensity at the line maximum I_0;

2) the integrated intensity I_∞, which is proportional to the area under the line;

3) "the half-width" of the line δ (Fig. 1).

All these quantities can be measured directly without difficulty.

The quantity δ characterizes the "width" of the line. In addition to this quantity the line width is characterized by an "effective width" δ_{eff}, which is defined by the relation (see reference 1):

$$\delta_{eff} = \frac{2}{\pi}\frac{I_\infty}{I_0}. \tag{1}$$

The factor $2/\pi$ is introduced to take account of the fact that for a true dispersion shape δ_{eff} and δ are the same. For line shapes of other kinds these quantities are not the same and the relation

$$r = \frac{\delta}{\delta_{eff}} \tag{2}$$

depends on the line shape. We shall call this factor r the "form factor," assigning it quantitative values. In spite of the fact that the numerical difference between δ and δ_{eff} is small, the form factor r turns out to be rather sensitive to variations in shape since the quantities δ and δ_{eff} are independent of each other and characterize lines with different skirts. The usefulness of this factor is the fact that it is very easily determined experimentally. hence for any observed line shape the true quantities (I_0, I_∞, δ) can be determined by means of simple measurements.

Knowing the form factor for the line shape being investigated it is easy to find an analytic expression which approximates the given shape. It is first necessary to use a "line-shape prototype." We use the following functions as prototypes:

1. A "slit" function, for the case in which the

TABLE I.

Function	Symbol	Half-width	I_∞	$\delta_{eff} = \dfrac{2I_\infty}{\pi I_0}$	$r = \dfrac{\delta}{\delta_{eff}}$
"Slit" function	$k_{1a}(x)$ $k_{1b}(x)$ $k_{1c}(x)$	$2s$ $2b$ $2b$	δ	$\dfrac{\delta}{(\pi/2)}$	$\dfrac{\pi}{2} = 1.57$
Gaussian function	$k_2(x)$	$2q\sqrt{\ln 2}$	$\sqrt{\pi}q$	$\dfrac{2q}{\sqrt{\pi}}$	$\sqrt{\pi \ln 2} = 1.47$
Dispersion function	$k_3(x)$	$2p$	πp	$2p$	1.0
$\dfrac{A}{(1+B)}\left[\dfrac{1}{1+\frac{x^2}{a^2}} + B\dfrac{1-\frac{x^2}{4a^2}}{\left(1+\frac{x^2}{4a^2}\right)^2}\right]$	$k_4(x)$	$2a$	$\dfrac{\pi aA}{1+B}$	$\dfrac{2a}{1+B}$	$1+B$

instrument slit is solely responsible for the line shape. Depending on the conditions of measurements this function has the following forms: a) rectangular, for the case of a spectrograph; b) trapezoidal, for a monochromator with input and output slits of different widths; c) triangular, for a monochromator with input and output slits of the same width.

2. A Gaussian function.

3. A dispersion function.

4. For curves which are spread out more than the dispersion curve, it is possible to use a function which we have proposed[2] with two parameters; one of these parameters characterizes the width and the other characterizes the departure of the line from a dispersion curve.

In Figs. 1 and 2 are shown these curves and in Table I are shown their characteristics.

It is apparent that the line-shape prototypes encompass a wide class of symmetric dome-shaped lines; asymmetric curves have been considered by us elsewhere[2] and will not be treated further here.
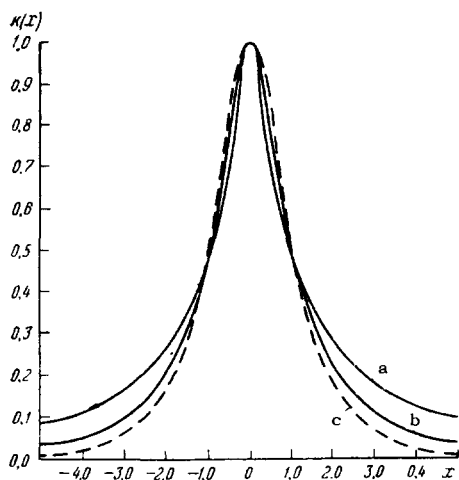
For intermediate values of r the observed line shapes can be represented by combination of the appropriate prototypes.

In practice the greatest range of interest lies between 2 and 3, since in the overwhelming majority of cases the observed Raman line shapes and exciting line shapes lie in this interval. In this case the shapes can be expressed analytically in terms of the Voigt function

$$k(X) = Ap \int_{-\infty}^{\infty} \frac{Ye^{-t^2}\,dt}{Y^2 + (X-t)^2}, \tag{3}$$

where $X = x/q$ and $Y = p/q$. This is a function with two parameters in which p characterizes the dispersion part and q the Gaussian part of the curve. These parameters can be easily determined for a given shape by measuring the values of I_0, I_∞, and δ. In particular, having determined the value of r from the experimental curve, we obtain from the curve in Fig. 3 the quantities $Y = p/q$ and $X_1 = x_1/q$ (x_1 is the abscissa cor-

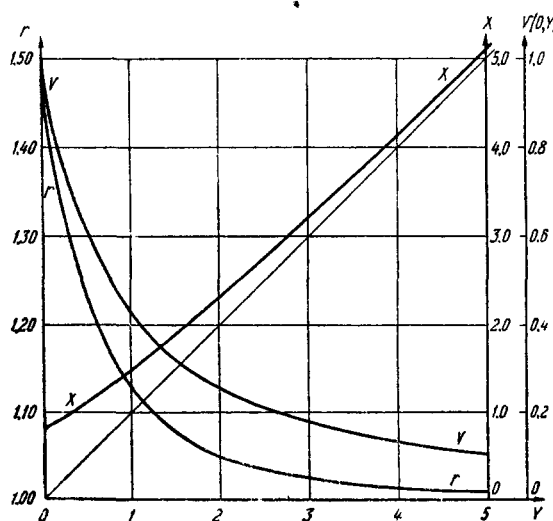FIG. 2. The function $k_4(x)$: a) B = −0.25; b) B = 0 (dispersion shape); c) B = 0.25.

FIG. 3. Graph for determining the parameters of the Voigt function from the observed line parameters.

responding to the half-width of the line). Whence

$$q = \frac{x_1}{X_1}, \quad p = qY.$$

After finding the approximating functions for the observed Raman line shapes and the exciting line shapes, the Raman line is found again in the form of a Voigt function, but with the parameters:

$$q_R = \sqrt{q^2 - q^2_{exc}}; \quad p_R = p - p_{exc}, \qquad (4)$$

where the quantities q_e and p_e refer to the exciting line.

Knowing p_R and q_R we find $Y_R = p_R/q_R$ (again from the curve in Fig. 3) $(X_1)_R$ and $r_R = r_{true}$. Whence, it is easy to find the true half-width of the Raman line

$$\delta_{true} = 2(x_1)_R = 2q_R(X_1)_R \qquad (5)$$

$$(\delta_{eff})_{true} = \delta_{true}/r_{true}. \qquad (6)$$

In Fig. 3 is also shown the function $V(0,Y)$ through which it is possible to determine the true intensity at the line maximum. Thus, all the parameters of the true shape are determined from the observed parameters of the Raman line and the exciting line by fairly simple operations. The appropriate mathematical apparatus has also been developed by us for the cases in which the observed shapes can not be expressed by means of the Voigt function.[3]

In the measurement of the integrated intensity, the problem of eliminating the distorting effects of the instrument and the exciting line can be solved fairly simply in principle, since the ratio of the integrated intensities of the Raman line does not depend on these factors. In practice, however, it is found that there is a general difficulty which is most important in measurements of integrated intensities.

In analyzing the spectrogram it is very important to take account of the fact that in practice we can trace the shape of the line only over a limited range, whereas in analytic form the line is given over an infinite interval. This situation is especially important in the investigation of Raman lines, which are wide and usually observed against a sizable continuous background. In favorable cases the Raman lines can be traced over a range of 5-6 "half-widths" δ; in most cases it is possible to carry out the trace over a range of 3-4 δ. In this case, the background, against which the intensity is reckoned, is taken between points amenable to observation; i.e., we isolate individual sections of the line and replace the complete shape by a "truncated" line shape (Fig. 4a). This substitution

leads to an error in the determination of I_∞, I_0, δ, and r; this error becomes larger for broader lines and smaller truncation widths.

As is apparent from Fig. 4a, the replacement of the line by a truncated line has the least effect on the quantity δ. If an interval not smaller than 4δ is used this error is less than several percent. Hence we can use the quantity δ_t measured with the truncated line for estimating the width of the interval. The corrections which must be introduced in going from the quantities $(I_0)_t$, $(I_\infty)_t$, δ_t, and r_t as determined from the truncated shape to the values of these quantities $(I_0)_c$, $(I_\infty)_c$, δ_c, and r_c for the complete line depend on the line shape. We compute these corrections for various values of the form factor r and various truncation widths. The pertinent results are given in the form of curves in Figs. 4b, c, and d. Using these curves, for a given width (in units of δ_t) it is easy to use the quantities $(I_0)_t$, $(I_\infty)_t$, δ_t, and r_t to find the values for the complete line. These corrections increase markedly at small widths; hence it is desirable to use an interval as wide as possible, in any case no less than 4δ.

The analysis of the true parameters of Raman lines is carried out by means of the examples described above.

We have considered in detail problems associated with the analysis of spectrograms and the elimination of distortions due to the instrument and exciting lines. However, these by no means exhaust the difficulties involved in the problem of measuring Raman-line intensities, since there are a number of factors which influence a given parameter. We may note that relative line intensities are always used so that a number of factors of geometric nature are automatically eliminated and the problem is simplified. The effects of the remaining factors vary, depending on the apparatus used and the measurement conditions.

We may note first that in comparing the intensities of Raman lines at different wavelengths it is necessary to take account of the variation in the sensitivity and transmission of the instrument at different portions of the spectrum. These factors can generally be taken into account without difficulty by calibrating the apparatus using a source with a known spectral energy distribution (see for example reference 1). Usually the literature gives values of intensities which are already corrected for the spectral sensitivity of the apparatus, and we shall not dwell on this problem in detail.

Raman spectra are usually obtained under fixed geometric conditions (a cell of definite size, fixed length for the illuminated part of the cell, fixed
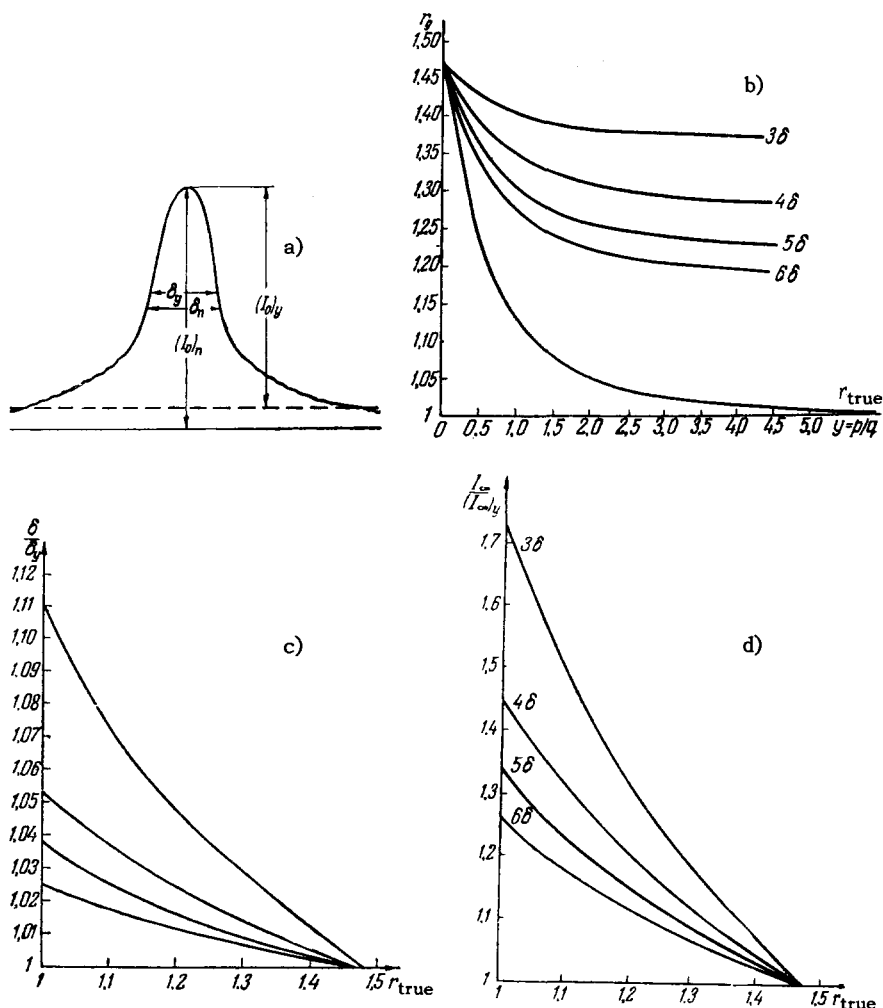
FIG. 4. Calculation of the "truncated" shapes for analysis of spectrograms: a) complete and truncated line shapes; b) curves for corrections to take account of the form factor r; c) curves for introducing corrections into the line width δ; d) curves for introducing corrections in the integrated intensity I_∞.

distance between the light source, condenser, and slit). Hence the scattering volume of the material being investigated remains fixed and the number of scattering molecules depends on the density d and the molecular weight M of the material being studied. However, it is necessary to take account of the fact that the intensity of the scattered light which is incident on the slit of the spectrograph depends on the index of refraction n of the material. Taking account of these factors we can give the intensity I′ of the Raman lines referred to 1 g-molecule of the material in the form

$$I' = c\,\frac{IMn^2}{d}\,F\,(n,\ \nu,\ \rho,\ \nu_{exc},\ T). \tag{7}$$

Here, I is the measured value of the intensity corrected for distortion introduced by the spectrograph and the exciting line as well as the spectral sensitivity of the apparatus; $F(n, \nu, \rho, \nu_e, T)$ is a factor that takes account of the relative effect of the index of refraction of the material, the frequency ν and depolarization ρ of the line being investigated, the frequency ν_e of the exciting line, and the temperature T; c is a constant that de-

pends on the choice of units. The problem of how to relate the intensity of a Raman line to a standard is discussed in greater detail at the end of this paper.

The factor F, which describes the effect on the intensity of the Raman line of the factors enumerated above, can be given in the form of a product

$$F\,(n,\ \nu,\ \rho,\ \nu_{exc},\ T) = f_1\,(n)\,f_2\,(\rho)\,f_3\,(\nu,\ T)\,f_4\,(\nu,\ \nu_{exc}). \tag{8}$$

We now consider each of the factors in this expression.

1. The effect of the index of refraction n on the intensity of the Raman lines is not completely described by the factor n^2 in Eq. (7). The index of refraction also has an effect on the reflection of light at the boundary between the glass and the material being investigated and consequently on the light flux that enters the material. The loss of exciting radiation because of reflection at the walls of the chamber depends strongly on the ratio of the indices of refraction of the material investigated and that of the glass walls. This factor has been considered in detail by Bernstein and Allen.[4]

TABLE II. Parameters of sources used to plot
Raman spectra.

Type of illuminator	β	γ	Δ	$f_2(\theta/\eta)/f_2(0)$
				for $\kappa=2$
With elliptical mirrors	0.5	0.1	0.05	1.09
With lamp focused on the cell by cylindrical lenses	0.0	0.1	0.0	0.81
Helix lamp	0.5	0.2	0.1	1.18

It appears to us that these authors have greatly overemphasized the role of this factor because, upon leaving the material, the exciting radiation is partially reflected in the backward direction into the cell and this tends to reduce the effect of the first reflection. These conclusions support experiments described by Sokolovskaya and Rautian[5] in which the intensity of Raman lines was investigated with the cell surrounded by a chamber containing alternately liquids with different indices of refraction. According to the estimates made in that paper, the corrections to the Raman line intensity due to reflection are less than 1% and may be considered negligible.

The effect of the index of refraction on the intensity of the Raman lines may also show up in the focusing properties of the cell and in a variation in reflection in the scattering volume at the slit of the spectrograph. According to the data of reference 5 the correction to the intensity due to these causes in photographic detection is negligibly small; i.e., we may assume that $f_1(n) = 1$. In photoelectric spectrographs the problem is somewhat more complicated as a consequence of the fact that sizable slit heights are used and the total internal reflection of the scattered radiation at the walls of the chamber becomes important. Thus, additional investigation will be required to evaluate the factor $f_1(n)$. Some of the uncertainty in the value of this factor in photoelectric detection can be avoided by using cells of special shape. Investigations along these lines are being carried out at the present time in our laboratory by G. V. Peregudov.

2. The effect of depolarization ρ of the Raman lines on the measured values of the intensities has been studied by a number of authors.[4,6,7] This problem has been investigated by us in detail. Preliminary work carried out in our laboratory[8] leads to the following expression for the pertinent factor in Eq. (8):

$$f_2(\rho) = \left\{ 1 + \gamma \frac{1-\rho}{1+\rho} \right.$$

$$\left. + (k-1) \left[\frac{\rho}{1+\rho} + \frac{1-\rho}{1+\rho}(\beta + \gamma - \Delta) \right] \right\}^{-1}. \tag{9}$$

Here k characterizes the polarizing effect of the spectrograph. If $J_{\parallel}$ and $J_{\perp}$ are the intensities of the components incident on the slit with the electric vector respectively parallel and perpendicular to the slit, whereas $J'_{\parallel}$ and $J'_{\perp}$ are the same components on exit from the apparatus,

$$\frac{J'_{\perp}}{J'_{\parallel}} = k \frac{J_{\perp}}{J_{\parallel}}. \tag{10}$$

The parameters β, γ, and Δ characterize the light source. If Oy is the direction of observation and the slit is parallel to Oz, (Fig. 5)

$$\begin{aligned} \gamma &= \overline{\cos^2 \vartheta}, \\ \beta &= \overline{\sin^2 \varphi}, \\ \Delta &= \overline{\cos^2 \vartheta \sin^2 \varphi}, \end{aligned} \right\} \tag{11}$$

where averages have been taken over all possible values of the angles, taking account of the distribution of intensity over angle. The parameters k, β, γ, and Δ can be determined experimentally. In Table II are shown the values of these parameters for certain typical cases.

When a spectrograph with $k \neq 1$ is used, the effect of depolarization can be minimized if the sample is illuminated uniformly in the plane perpendicular to the direction of observation $(\beta = \frac{1}{2})$. This condition is usually more or less satisfied in standard light sources with elliptical reflecting walls or when helix lamps are used. It is also necessary that the illumination be concentrated primarily in the direction perpendicular to the axis
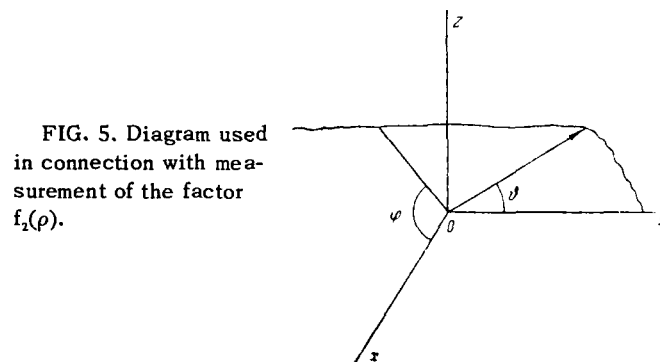
FIG. 5. Diagram used in connection with measurement of the factor $f_2(\rho)$.

of the cell (small values of γ and Δ). This condition is also satisfied in standard elliptical sources (see Table II). Therefore, when one works with sources of this kind the maximum depolarization correction is generally less than 10% and can be easily taken into account even if the value of ρ is not known accurately.

If sources are used in which the lamp is focused on the cell by cylindrical lenses, the correction may become quite significant (see Table II), and it is important that the correction be taken into account. In this connection it should be noted, to avoid misunderstanding, that the correction formula of reference 4 is valid only if one takes ρ to mean the observed depolarization under certain conditions, namely $\beta = 0$ (in apparatus with a polaroid at the scattering cell, we have as an additional condition k = 1).

3. Generally speaking the values of Raman line parameters depend on temperature. The temperature dependence of the intensity of Raman lines does not agree with the expression

$$I \sim \left[1 - \exp\left(-\frac{hc\nu}{kT} \right) \right]^{-1}, \tag{12}$$

derived from the elementary theory of the effect. Hence it hardly makes sense to introduce the factor (12) in the intensity formula, as was done in reference 4.

An investigation of the "anomalous" dependence of the parameters of Raman lines on the temperature has been carried out in a number of papers by Ya. S. Bobovich and his co-workers,[9] by A. I. Sokolovskaya and P. A. Bazhulin,[10] A. V. Rakov,[11] N. I. Rezaev,[12] and others. For purposes of illustration, we present in Table III data for several lines in benzene and cyclohexane. It is evident that the parameters of the Raman lines vary with temperature in a rather complicated way; apparently the most stable parameter is the integrated intensity. In view of the absence of any theory for this effect, we suggest that at the present time it is best to standardize the conditions of measurement. In accordance with this suggestion, in reference 1 all data refer to a temperature of 30°C. For the small variations of temperature generally encountered in experimental work, say ±10°, changes in intensity are small and can be neglected. For greater changes in temperature the appropriate factor $f_3(\nu, T)$ must be determined experimentally for each line.

4. In the majority of cases the factor that accounts for the frequency dependence of the intensity of the Raman lines can be given in the form

$$f_4(\nu, \nu_{exc}) = \frac{1}{(\nu_{exc} - \nu)^4}. \tag{13}$$

However, in cases in which ν_{exc} is close to the frequency of an electronic transition ν_{el} (for example in compounds with conjugated shortened bonds) this formula becomes inconvenient. A large number of papers have been devoted to studies of the dependence of the intensity of Raman lines on the frequency of the exciting light (see for example references 13-16). Without dwelling on the details we may note that this dependence can be taken account of approximately by replacing Eq. (13) with the semi-empirical expression

$$f_4(\nu, \nu_e) = \frac{[(\nu_{el}^2 - \nu_e^2)^2 + 4\gamma^2\nu_{el}^2]^2}{(\nu_e - \nu)^4 (\nu_{el}^2 + \nu_e^2)^2}, \tag{14}$$

in which the constants ν_{el} and γ must be determined from experiment for a given vibrational frequency ν.

In the foregoing analysis we have not distinguished between photographic and photoelectric detection systems in taking account of the effect of various factors on the measured values of Raman line intensities. These two methods of measuring intensities have certain distinguishing features, but these will not be considered here. Thus, we assume that it is possible to obtain reproducible values of the intensities of the Raman line which can serve for the purpose of molecular spectral analysis and for the solution of problems of theoretical nature.

In conclusion we consider the problem of units for measuring intensities of Raman lines. In our

TABLE III. Dependence of Raman line parameters on the temperature.

Material	$\Delta\nu$	$t°$ C	J_∞	I_0	δ
Cyclo-hexane	802	+20	100	250	2.1
		+70	96	205	2.2
	1029	+20	100	110	10.5
		+70	82	79	14.2
	1267	+20	100	98	10.8
		+70	86	72	14.8
	1445	+20	100	92	13.2
		+70	84	68	16.9
Benzene	607	+20	100	100	6.6
		+70	98	73	9.2
	992	+20	100	100	1.7
		+70	70	61	2.1
	1586	+20	100	100	12.5
		+70	95	70	17.9
	1606	+20	100	100	8.8
		+70	99	77	11.4

work we always use an intensity scale in which the intensity at the maximum of the cyclohexane line 802 cm^{-1} is taken as 250 units. The integrated intensity of this same line is taken as 500 units, and since the given line has a true dispersion shape while its half-width is $\delta = 2$ cm^{-1},

$$\delta = \delta_{eff} = I_\infty/I_0.$$

If the total intensity of the Raman lines is expressed on the scale indicated here, the ratio I_∞/I_0 is numerically equal to the effective half-width of the line δ_{eff} expressed in cm^{-1}. We may note that the extremely simple relation between the quantities I_∞, I_0, and δ_{eff} is a consequence of the fact that the cyclohexane line at 802 cm^{-1}, chosen as the standard, has a true dispersion shape. For a line with a complicated shape, for example for the 459 cm^{-1} CCl_4 line, these relations are not satisfied. Hence, if the 459 cm^{-1} CCl_4 line is used as a standard it is necessary to introduce two independent (or artificially related) intensity scales: one for the quantity I_0, the second for the quantity I_∞; this is obviously inconvenient. Other considerations which dictate against the use of the 459 cm^{-1} line as a standard are given in reference 1 and we will not discuss them here.

Inasmuch as the data in many papers are still given in terms of the 459 cm^{-1} CCl_4 line, we have found it necessary to investigate the parameters of this line carefully. The values for the integrated intensities are as follows:

$$\frac{I_\infty (459)}{I_\infty (802)} = 2.9.$$

For the "reduced" intensity I', in accordance with Eq. (7) we have

$$\frac{I'_\infty (459)}{I'_\infty (802)} = 2.7.$$

In these measurements we have used the diffraction-grating spectrograph described in reference 17. The analysis of the experimental data was carried out by means of the methods described in the present paper.

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