

MODERN TECHNICAL MEANS AND METHODS OF STUDYING RAMAN SPECTRA

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1. INTRODUCTION

GREAT advances in Raman spectroscopy have been concerned with the measurement of the vibrational frequencies. However, the electrooptic parameters of the spectrum (the intensity and polarization of the bands) also contain highly valuable information on the composition and structure of matter. This has been made especially accessible through the rapid development of the photoelectric technique of measuring spectra and the invention of new spectroscopic instruments, excitation sources, and methods of study. It is precisely because experimenters have had access to sufficiently refined apparatus that thorough solutions could be found for such "old" problems as the study of scattering in gases and powders. These problems play a very great role in the determination of certain molecular characteristics, as well as with regard to various aspects of the problem of intermolecular interaction. Intensive work has begun on the problems of resonance Raman scattering, a phenomenon lying at the borderline between two fields of spectroscopy (scattering and luminescence), and hence one extremely important in understanding the nature of the interaction of light with matter. The results obtained here have found interesting applications in structural studies of complex organic compounds. The possibility has arisen of a broad study of various glassy systems. Finally, new lines of research have appeared: spectroscopy of stimulated scattering, of fast processes, of colored substances, and under high resolving power; these show great promise of further development and varied applications.

All the circumstances noted above bring to the fore the problem of describing the new experimental technique and methods of study used in Raman spectroscopy. On the other hand, the marked increase in the precision of measurements also compels us to concentrate our attention on the problem of how to take into account various factors capable of distorting the physical meaning of the quantities being measured. This review is intended to serve these purposes. Here most of the space will be taken up with those problems that have been poorly reflected, or not at all, in the prior review literature, or that have undergone a new essential development in recent years, or finally, that are open to an alternative interpretation. They include the description of modern photographic and photoelectric apparatus, of all the possible spectral excitation sources and methods of power supply for them, of

methods of studying powders, and gases and vapors at moderate and high pressures, and the analysis of the conditions for obtaining correlatable band-intensity values, and in particular, how to take into account the effect of the refractive index of a liquid medium on the measured values, and certain other problems. An account of other aspects of the problem can be found in review and original articles.^[1-15]

2. THE INTENSITY AND DEGREE OF DEPOLARIZATION OF RAMAN BANDS IN A GASEOUS MEDIUM

General considerations on the Raman-scattering phenomenon imply that the electrooptical properties of spectra, the intensity and polarization of the bands, depend on a number of molecular characteristics.^[16,17] In the semiclassical theory of the phenomenon, one usually works with a quantity that effectively takes into account these characteristics, the derivative α' of the polarizability with respect to the normal vibrational coordinates. For anisotropic molecules, this is a tensor quantity defined by the following invariants, the so-called trace:

$$a' = \frac{\alpha'_1 + \alpha'_2 + \alpha'_3}{3} \quad (1)$$

and the anisotropy:

$$b' = \sqrt{\frac{1}{2} [(\alpha'_1 - \alpha'_2)^2 + (\alpha'_2 - \alpha'_3)^2 + (\alpha'_3 - \alpha'_1)^2]}, \quad (2)$$

where α'_1 , α'_2 , and α'_3 are the values of the derivatives of the polarizability with respect to three mutually perpendicular directions (the "principal values" of α'). In observing the scattering at an angle of $\pi/2$ to the direction of illumination, the intensity of the bands is proportional to a certain combination of the invariants of the tensor α' :

$$I_{\pi/2} \sim (45a'^2 + 13b'^2). \quad (3)$$

However, the actual instruments used to obtain Raman spectra are distinguished by their large aperture for the exciting light. This is how one obtains efficient illumination. Strictly speaking, we cannot always consider even the aperture of the scattered beam utilized by the spectroscopic instrument to be negligibly small. Hence, as a rule, we must take into account the angular distribution of the scattering intensity. According to Placzek^[16], see also^[18], for a parallel beam this distribution will have the form

$$I_\varphi = I_{\pi/2} \left(1 + \frac{1 - \epsilon_{\pi/2}}{1 + \epsilon_{\pi/2}} \cos^2 \varphi \right), \quad (4)$$

where φ is the angle at which the observation is made,

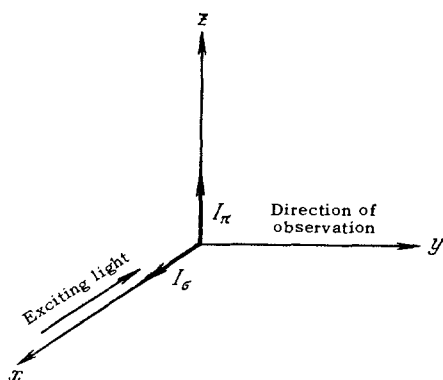


FIG. 1. Geometry of an idealized Raman-scattering experiment.

and $\rho_{\pi/2}$ is the true depolarization of the Raman scattering band.

In order to grasp the physical meaning of the latter quantity, let us consider the idealized experimental system in Fig. 1. Let the exciting (natural) light be incident on the system in the direction of the x axis, and the observation be made along the y axis. Let us resolve the scattered light with a suitable analyzer (a Wollaston or Osipov prism, or polaroid films) into two components, one of which has the electric vector oscillating along the z axis, and the other along the x axis (the π - and σ -components). According to calculation, the following relation will hold for a system of freely oriented molecules:

$$\frac{I_{\sigma}}{I_{\pi}} = \rho_{\pi/2} = \frac{6b'^2}{45a'^2 + 7b'^2}. \quad (5)$$

Further, it turns out that $\rho_{\pi/2}$, the depolarization of the Raman bands, can vary only within relatively narrow limits (from 0 to $\frac{6}{7}$). These values characterize the type and symmetry of the vibrations, as well as the symmetry of the equilibrium configuration of the nuclei.

If the actual apparatus with which the study is being performed is distinguished by having a large aperture for illumination only along the axis of the cuvette, then the angle φ in Eq. (4) will take on the meaning of a certain mean effective angle $\bar{\varphi}$. In this case, the intensity of the bands will be described by the expression

$$I_{\bar{\varphi}} \sim (45a'^2 + 13b'^2) \left(1 + \frac{1 - \rho_{\pi/2}}{1 + \rho_{\pi/2}} \cos^2 \bar{\varphi} \right), \quad (6)$$

which can be used in practice after a preliminary measurement of the depolarization $\rho_{\pi/2}$ and the effective angle $\bar{\varphi}$. The method of determining the latter quantity will be discussed below.

However, there are other, more practical ways of solving the problem of measuring the band intensities that are free from the effect of the distorting factors of the type under discussion. One of these was proposed by Bernstein and Allen.^[19] By a simple transformation, we can easily prove the identity

$$(45a'^2 + 13b'^2) \equiv (45a'^2 + 7b'^2) (1 + \rho_{\pi/2}). \quad (7)$$

Substituting (7) into (6), we have

$$I_{\bar{\varphi}} \sim (45a'^2 + 7b'^2) (1 + \rho_{\pi/2}) \left(1 + \frac{1 - \rho_{\pi/2}}{1 + \rho_{\pi/2}} \cos^2 \bar{\varphi} \right). \quad (8)$$

According to the calculations of Martin,^[19] the depolarization $\rho_{\bar{\varphi}}$, as measured by the classical method (with an analyzer in the scattered light beam) in a wide-aperture instrument satisfying the condition noted above, is related to the invariants of the tensor α' and the angle $\bar{\varphi}$ by the equation

$$\rho_{\bar{\varphi}} = \frac{3b'^2 (1 + \sin^2 \bar{\varphi}) + (45a'^2 + 4b'^2) \cos^2 \bar{\varphi}}{45a'^2 + 7b'^2}. \quad (9)$$

By solving Eqs. (5), (6), and (9) simultaneously, we obtain the following simple expression:

$$I_{\bar{\varphi}} \sim (45a'^2 + 7b'^2) (1 + \rho_{\bar{\varphi}}). \quad (10)$$

To transform to the intensity at the exit point of the apparatus, i.e., to the quantity directly measured experimentally, we must introduce the coefficient K , which characterizes the total polarizing action of the spectroscopic instrument and the photocathode of the detector:

$$\rho'_{\bar{\varphi}} = K \rho_{\bar{\varphi}}. \quad (11)$$

Thus, we have reduced the solution of the problem being posed, that of obtaining correlatable intensity values, to a single supplementary, relatively simple measurement of the depolarization $\rho_{\bar{\varphi}}$, as distorted by the finite longitudinal aperture of the exciting beam of light in the apparatus being used. This is the gist of the method of Bernstein and Allen.^[19]

Being rather simple, the Bernstein-Allen method also permits one to improve the accuracy of the measurements somewhat over that of the previously described method, which requires data on $\rho_{\pi/2}$ of the bands and on $\cos^2 \bar{\varphi}$ of the apparatus. Indeed, Eq. (9) can be written in the following form:

$$\rho'_{\bar{\varphi}} = K (\rho_{\pi/2} \sin^2 \bar{\varphi} + \cos^2 \bar{\varphi}). \quad (12)$$

We see that there is a linear relation between the quantities $\rho'_{\bar{\varphi}}$ and $\rho_{\pi/2}$. At values $K > 1$, the scale of the measured quantities is practically unshortened. Consequently, since the efficiency of a wide-aperture polarization apparatus is greater than that of a narrow-aperture apparatus, the precision of the depolarization measurements is increased, as well as the precision of measurement of the band intensity $I_{\bar{\varphi}}$. Equation (12) directly gives rise to a method of determining the quantity $\cos^2 \bar{\varphi}$.

In order to illuminate the sample still more intensively in measuring the depolarization, we could try to increase also the transverse aperture of the light beam. However, this method proves to be impractical in the classical polarization apparatus, since it leads to a shortening of the range of possible values for ρ'_{var} . There is another method of measuring the depolarization that is free from this defect, and has been very widely applied in recent years.^[20-22] In essence, it consists in the following.

Two measurements are made in succession. In one of these, the cuvette is wrapped in a polaroid film rolled in the form of a tube, transmitting light having its electric vector parallel to the cuvette axis; in the other, the electric vector is in the perpendicular plane. Calculations show that the ratio of the corresponding quantities is equal to $\rho_{\pi/2}$, provided only that the aperture of the light is limited along the cuvette. When the cuvette is illuminated from all directions, $(\rho_{\text{var}})_{\text{tr}}$ is given by Eq. (12). The latter fact, that one can use illumination from all directions, is the reason for the high efficiency of this method, permitting one to increase the accuracy of the measurements. Hence, it is convenient to replace the quantity ρ_{φ} in Eq. (12) by $(\rho_{\text{var}})_{\text{tr}}$. As is shown by simple considerations,^[21,23] it even suffices to use alone the polarization component having the electric vector perpendicular to the axis of the cuvette. The conditions under which these results are applicable will be formulated below.

A study by Naberukhin^[24] has greatly clarified the details of the problem of the effect of the illumination geometry on the measured intensity of the lines. By considering together the illumination geometry, the losses due to reflection of light at the air-glass interface of the cuvette, and the polarizing action of the spectroscopic apparatus, Naberukhin showed that the intensity of a line in the general case can be written as a complicated function of four effective parameters of the light source, the quantity K , and the true depolarization $\rho_{\pi/2}$:

$$I \sim (45a'^2 + 13b'^2) \left\{ 1 - \frac{1-\delta}{1+\rho_{\pi/2}} + \frac{1-\rho_{\pi/2}}{1+\rho_{\pi/2}} \gamma + (K+1) \times \left[\frac{\rho_{\pi/2}}{1+\rho_{\pi/2}} \frac{\delta+1}{2} + \frac{1-\rho_{\pi/2}}{1+\rho_{\pi/2}} (\gamma + \beta - \Delta) \right] \right\}. \quad (13)$$

For a scale based on the quantity $45a'^2 + 7b'^2$, Eq. (13) is transformed into:

$$I \sim (45a'^2 + 7b'^2) \left[1 - (1-\delta) \left(1 - \frac{\rho_{\pi/2}}{2} \right) - (1 + \rho_{\pi/2}) (\beta - \Delta) \right] (1 + \rho_{\varphi}^c). \quad (14)$$

When $K = 1$ (non-polarizing instrument), Eq. (13) is considerably simplified:

$$I \sim (45a'^2 + 13b'^2) \left\{ 1 - \frac{1-\delta}{1+\rho_{\pi/2}} + \frac{1-\rho_{\pi/2}}{1+\rho_{\pi/2}} \gamma \right\}, \quad (15)$$

which differs from Eq. (6) only in the term $(1-\delta)/(1+\rho_{\pi/2})$, which characterizes the effect of the reflection losses. In^[24], a procedure is described for determining the parameters β , γ , δ , and Δ , and their numerical values are given for typical light sources. All of this permitted the author of^[24] to determine the limits of applicability of the above-discussed corrections to the measured intensities of bands. In particular, he showed that the condition under which one can use the value $(\rho_{\text{var}})_{\text{tr}}$ in Eq. (10), or simply the

polarization component having its electric vector perpendicular to the cuvette axis, is that the illumination should be uniform in the (x, z) plane ("around the cuvette"; see Fig. 1). This requirement is precisely the one realized in the most widely applied light sources: the elliptical ones, and those having helical lamps and scattering screens.

In trying to obtain standard intensity values in the general case by use of Eqs. (13) and (14), we must not lose sight of the precision with which the parameters entering into it have been determined. If we start with the fact that the mean accuracy of intensity measurement amounts to $\pm 1\%$ and also take into account the specific errors of the polarization measurements, then the accuracy of the determination of the parameters proves at best to be $\pm 10\%$. This leads to an even greater deviation in the intensity values. Hence, in many cases the introduction of additional parameters is not worthwhile. That is, the increase in precision of the measured intensity will be illusory.

Conclusions. Precise values of the intensity, from which the effect of the depolarization of the bands and the illumination geometry has been eliminated, can be conveniently obtained by use of standard apparatus of known illumination geometry.

In principle, we could use for this purpose an illuminator consisting of two linear lamps in a horizontal position, without limitation of the longitudinal aperture, and at a distance from the cuvette such that the transverse aperture of illumination is no greater than about 10° . This would introduce a correction factor into the results of the measurements in the form of the factor $(1 + \rho_{\varphi}^c)$, according to Bernstein and Allen. However, such an apparatus does not have a great light efficiency, since it rules out the use of reflecting and scattering screens, as well as spectrographs having a large relative camera aperture. The correction factor itself in such a simple form is valid only for non-polarizing instruments.^[24]

There is a method completely free of all the cited defects; here the measurements are always performed with a polaroid tube included in the beam of exciting light so as to transmit light having its electric vector in the plane perpendicular to the axis of the cuvette. The only condition required for applicability of this method is uniform illumination of the sample from all sides, as is easily realized in practice. For these reasons, this method is unconditionally to be preferred.

3. THE INTENSITY AND DEGREE OF DEPOLARIZATION OF RAMAN BANDS IN LIQUIDS

Liquid scattering media are characterized by a rather broad range of refractive-index values. The latter can affect the intensity of the scattered light that actually reaches the detector. In general, the relation between the intensity and the refractive index arises

from the combination of a series of optical effects and intermolecular interactions; it is complex and not amenable to exact quantitative calculation, and cannot be written in analytic form. In certain studies, the major role has been ascribed to some one of the factors to the neglect of all the others.^[19,23,25,26,11] A number of authors have used different terms to describe the same phenomenon, introducing confusion into the interpretation of the results.^[25-27] Errors of theory are also encountered in the analysis of the problem. The topic of this section will involve an attempt to discuss the problem as a whole.

A. Optical Effects

These effects comprise the behavior of both the exciting light and the scattered light. Before it enters the liquid medium from the air, the beam of exciting light is partially reflected at the boundary with the glass of the cuvette. However, the corresponding light losses are constant for a given type of glass, and they are of no interest to us in this case. However, the reflection at the other "glass cuvette-liquid" boundary will depend on the refractive index of the liquid, and in principle can distort the measured quantities. However, some simple considerations pointed out by Rea,^[25] as well as the direct measurements of Sokolovskaya and Rautian,^[26] show that in actual cases the magnitude of the losses due to this reflection is negligibly small.

Another factor relating to the exciting beam involves its geometry within the cuvette. For an element of volume, the efficiency of scattering will be determined by the illumination of the substance. It does not depend on the refractive index n_{liq} . However, if we are considering a cuvette of finite dimensions, we must consider the length of the rays, which undergo refraction at the boundary with the liquid. This fact has been taken into account by Rea^[25] under the idealized conditions of illumination of a cylindrical cuvette, in which the light aperture along the cuvette is limited with diaphragms ("the planar case"). Calculation has shown that the efficiency of excitation is proportional to n_{liq} .*

One ordinarily does not use limiting diaphragms in measuring the intensity of bands in spectra. Hence, in general one must also take into account the effect of the longitudinal aperture as well. Here, as is known, the length of the refracted rays along the cuvette will evidently decrease with increasing n_{liq} . Hence, the effect of the same type in the cross-sectional plane of the cuvette can be at least partially compensated.

V. P. Kozlov has carried out a complete mathematical analysis of this problem. He considered an elliptical cross-section of a cylindrical cuvette under uniform illumination from all sides. It turned out that under these actual conditions, the mean length of the

refracted rays does not depend on the refractive index of the medium. This also proved that one need not introduce any correction factors for the change in the geometry of the exciting beam in the liquid.

The situation differs in the geometry of the scattered beam: it requires the introduction of corrections. We can approach this problem from two standpoints. In the first of these, we take into account the sudden change in the intensity of the beam upon emergence into the air, which is the photometric quantity of importance in the spectrum being recorded. The corresponding coefficient is $1/n_{liq}^2$. Hence, in order to obtain correlatable band-intensity data, we must multiply the measured quantities by n_{liq}^2 .^[28,36] The other approach to the problem is based on considering the effective volume of the cuvette, i.e., the volume "visible" to the spectroscopic apparatus. Calculations show that the apparatus transmits only a fraction of $1/n_{liq}^2$ of the emitted light flux.^[27,25] The result is the same as that derived above.

For photoelectric measurement of the emission, spectrometers are commonly used that have slits very long in comparison with the diameter of the cuvette.^[29,22] At the same time, having a limited amount of material, one uses to advantage long and narrow cuvettes. Under these conditions, in addition to the direct rays, others also enter the apparatus that have undergone one or several total internal reflections within the cuvette containing the liquid. An attempt is made below to take into account the corrections for the variation in the refractive index involving the contribution from total reflection to the measured light flux.

First of all, it is essential to determine how large this contribution is. Such a calculation has been made for reflection at the air interface of the meridional rays (i.e., those lying in the mid-section) in a study by Slyusarev and Chulanovskii.^[30] It turned out that with actually realizable dimensions of the cuvette, the utilization of the reflected light can increase the flux reaching the detector several-fold. If we consider not only the meridional but also the oblique rays (i.e., those not intersecting the axis of the cuvette), the efficiency of energy transfer along the cuvette will be even greater. The theory of this problem can be adapted from the studies concerned with the propagation of light in a fiber (see, e.g.,^[31]).

Figure 2 shows the geometry of the total internal reflection at the interface between two media. From Snell's law we can directly derive

$$I \sim \sin^2(\Theta - \varphi_{crit}) = \frac{n_1^2 - n_2^2}{n_1^2}, \quad (16)$$

which gives an approximate measure of the transmittable energy.* We see that as n_1 increases (for a

*The fact that the two quantities vary in the same direction is obvious even without calculation, while the simple proportionality arises from the simplifications assumed in^[25]

*In the fiber-optics studies, the analogous relation is written in the form $n_1^2 - n_2^2$. The denominator drops out when we take into account the sudden change in the intensity of the beam on entering the fiber from the air.

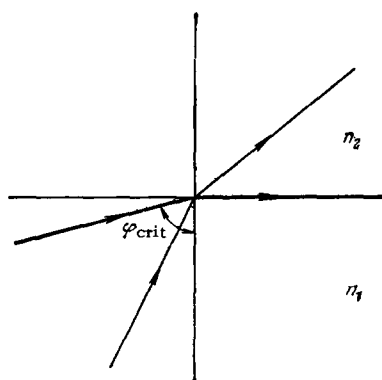


FIG. 2. Geometry of the total internal reflection at the boundary between two media.

fixed value of n_2), the fraction of the light reflected into the denser medium increases. The dependence is especially marked in the case when n_1 and n_2 do not differ greatly.

In considering a real cuvette, we must bear in mind the fact that the light flux from total reflection will consist of two parts when $n_{liq} > n_{glass}$.^{*} One of them is due to reflection at the liquid-glass interface, and the other at the glass-air interface. It is precisely the first part that depends on the refractive index of the liquid in accordance with Eq. (16). One can easily show that even this part of the flux can be comparable with the flux incident directly on the spectroscopic apparatus.

The goal of the treatment below will consist in estimating the effect of the refractive index of the liquid on the results of measurement of the total light flux. If we assume that the contributions of the reflected and direct fluxes are equal, we have

$$\Phi \sim \frac{1}{n_{liq}^2} \frac{n_{liq}^2 - n_{glass}^2}{n_{liq}^2} + \frac{1}{n_{liq}^2} = \frac{1}{n_{liq}^2} \left(\frac{2n_{liq}^2 - n_{glass}^2}{n_{liq}^2} \right) \quad (17)$$

(the additional factor $1/n_{liq}^2$ preceding the first term takes into account the change in intensity of the reflected beam upon exit from the cuvette). We can easily convince ourselves that for a typical case, where $n_{glass} = 1.5$, $n_{liq}' = 1.6$, and $n_{liq}'' = 1.7$, the factor governing the effect of the refractive index on the quantity Φ practically remains constant. Of course, mutual compensation cannot occur in working with very narrow cuvettes. In such cases, as n_{liq} increases one will get increased values of the measured intensities, owing to the optical effects.

B. Intermolecular Interaction

Owing to the specific intermolecular interactions in the condensed state of matter, both the polarizability

^{*}The situation differs when $n_{liq} < n_{glass}$. However, the treatment in this case leads to the same results with regard to the role of n_{liq} .

itself and its derivatives with respect to the vibrational coordinates can vary. The latter is expressed in the behavior of the intensities of the Raman bands.^[32a] The theory of this problem has not yet been worked out. However, as we know, it is clear that generally the antisymmetric, unpolarized vibrations will be especially strongly affected by intermolecular forces. The intensities of these vibrations are determined by the anisotropy of the tensor α' . As a rule, the latter depends on the squares of the small differences between the principal values of α' [Eq. (2)].

However, if even the derivative of the polarizability does not depend much on the medium, we must always still take into account the universal phenomenon of the variation of the field intensity of the light wave on going from one medium to another. We can take this factor into account on the basis of the concept of the internal field of the substance. It has been possible on this basis to explain many of the peculiarities of absorption and emission spectra.^[32b,34] It has been quite proper to try to apply analogous corrections to the results of Raman-spectrum measurements as well. The possible effect of the internal field is mentioned in a study by Woodward and George.^[27] Pivovarov^[35] has taken this effect into account in semi-quantitative form.

The study of Pivovarov^[35] involves an anisotropic vibrating molecule situated in a medium having a refractive index n . If we start with the internal field as given by Onsager, the effective values of each of the principal polarizabilities of such a molecule can be expressed as follows:

$$\alpha_{eff} = \frac{3n^2 ar^3}{(2n^2 + 1)r^3 - 2(n^2 - 1)\alpha}, \quad (18)$$

where r is the radius of the Onsager region.^[36] Differentiating α_{eff} with respect to the vibrational coordinate, we have:^{*}

$$\alpha'_{eff} = \frac{3n^2 (2n^2 + 1)r^6}{[(2n^2 + 1)r^3 - 2(n^2 - 1)\alpha]^2}. \quad (19)$$

The square of this expression determines the relation of the intensity of the Raman band of the diatomic molecule to the refractive index n . In order to determine the behavior of polyatomic molecules, we must solve the mechanical and electrooptical problems for them. In the typical case where $\alpha/r^3 = 0.5$, $n_1 = 1.35$, and $n_2 = 1.5$, the ratio $(\alpha'_{2,eff}/\alpha'_{1,eff})^2$, which approximately characterizes the ratio of intensities of the corresponding bands, amounts to 1.25. This quantity can be easily measured.

Another approach to the estimation of the possible effect of the refractive index of the substance on the intensity of Raman bands has been noted in^[25,37,38]. The authors of these studies apply to the light-scattering case an expression describing the relation of the intensity of absorption bands to the refractive index that has been repeatedly used in the literature:

^{*}There is an error in^[35]: the denominator hasn't been squared.

$$\frac{I_{\text{liq}}}{I_{\text{gas}}} = \frac{(n^2 + 2)^2}{9n} \quad (20)$$

As we see, Eq. (20) contains no parameters specific to the molecules being studied; in the opinion of Girin and Bakhshiev,^[34] the latter involves erroneous initial assumptions. A critical analysis of the problem as a whole can be found in the review^[34].

It would seem at first glance that we could decide which of the intensity expressions is correct by comparing the data of measurements in the liquid and vapor phases of a substance. In actuality, however, this is not true. The trouble is that the results of the comparison depend on the temperature of the substance. Thus, for example, in the study by Sokolovskaya^[39] the measurements on the liquid were performed at a temperature of +20°C, while those on the vapor were performed at +120°C. Upon extrapolating the behavior of the liquid to the experimental conditions under which the vapor was studied, Sokolovskaya obtained a value of about 1.5 for the intensity ratio. However, by the same reasoning we can refer the vapor to the experimental conditions for the liquid. Then we get a value about twice as great for the same ratio. Thus, the most quantitative treatment of the pertinent data contains an inevitable indeterminacy and arbitrariness, preventing us from drawing any conclusions on the nature of the internal field in the substance. From the mathematical standpoint, this is a situation of a single equation with two unknowns.

However, a rather voluminous experimental material has been accumulated at present on the behavior of the intensity of Raman bands as a function of the type of solvent^[25,37,40-44] and the temperature of the substance,^[46-51] which directly reflects the influence of the internal field. It has turned out that an increase in the refractive index, regardless of how attained, invariably strengthens the bands. We can also consider it established that in a number of cases different vibrations in the same molecules behave in different ways.^[40,41,37] Strongly polarized skeletal vibrations sometimes do not vary appreciably in intensity, while the depolarized vibrations undergo considerable changes. We can see the latter from the graphs in Figs. 3 and 4. The experimental data also reflect quite distinctly the specific characteristics of the molecules. All these facts indicate the reality of the influence of

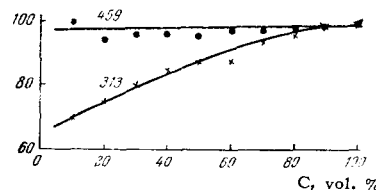


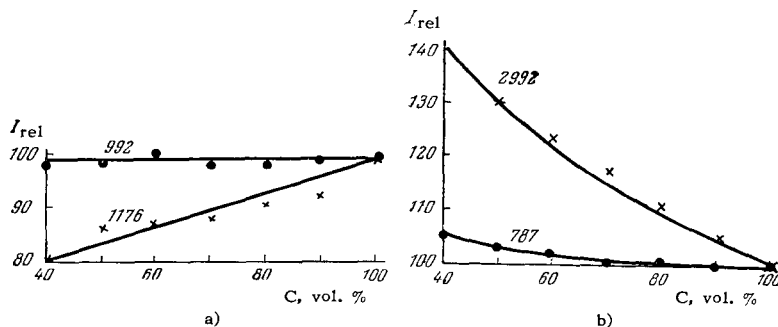
FIG. 3. The relation of the molar integral intensity coefficients of the 459 and 313 cm^{-1} bands of carbon tetrachloride to its volume concentration in mixtures with acetone.^[41]

the universal interaction, which can be described in terms of the refractive index of the substance, e.g., by Eq. (19).

However, the problem is not finished with taking into account the universal interaction involving the refractive index of the substance. Other types of interactions are also possible, e.g., those due to the existence of dipole moments in the molecules being studied (or the existence of varying dielectric constants in the solutions). As the measurements of T. P. Tulub have shown, one observes certain definite regularities in the behavior of the band intensities in this case as well. A most essential fact bearing on this problem consists in the especial role of the totally-symmetric vibration at 459 cm^{-1} in the spectrum of carbon tetrachloride: as before, it varies little or not at all in intensity as a function of the concentration of the solution (Figs. 5 and 6).

Since an overall account of the optical effects that can distort the physical meaning of the measured intensity values is generally not amenable to theoretical analysis, Sokolovskaya et al.^[26] have proposed a procedure for the separate determination of these effects. Unfortunately, we cannot yet estimate in this way the contribution from total internal reflection. However, the set of observations made above suggests a simple (although far from irreproachable) solution of the problem. Obviously, it must amount to calibrating the apparatus with artificially-prepared mixtures of various concentrations of carbon tetrachloride with a substance having a considerably different refractive index (e.g., acetone). This is precisely what the authors of^[41] have done. The approximate constancy of the intensity of the 459 cm^{-1} band established in^[41] can be taken as the basis of the analysis performed above of

FIG. 4. The relation of the molar integral intensity coefficients of the 992 and 1176 cm^{-1} bands of benzene (a) and the 2992 and 787 cm^{-1} bands of acetone (b) to the volume concentrations of these substances in benzene-acetone mixtures.^[41]



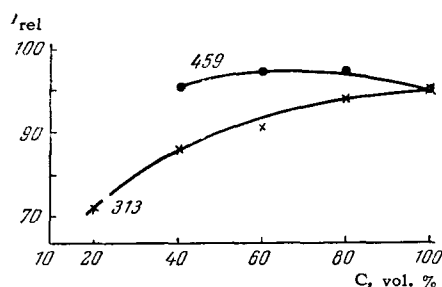


FIG. 5. The relation of the molar integral intensity coefficients of the 459 and 313 cm^{-1} bands of carbon tetrachloride to its volume concentration in mixtures with cyclohexanol. The refractive indices of the components of the mixture are approximately equal, but the dielectric constants differ considerably (2.24 and 15 for carbon tetrachloride and cyclohexanol, respectively).

the role of total internal reflection in the cuvette. It is a feature of the apparatus in [41].

C. The Effect of Certain Other Factors on the Band Intensities

In comparing the intensities of vibrations in different molecules, we must in general take into account the effect of the frequency of the exciting light, as well as that of the absorption band responsible for the act of Raman scattering. It is generally considered that the intensities of the Stokes-region bands in Raman spectra are proportional to the quantity $(\nu_e - \nu_v)^4$, where ν_e and ν_v are the frequencies of the exciting and the vibrational lines, respectively. However, this relation has been disputed recently. [52,53] Furthermore, there are some experimental data that are difficult to fit to it. [52-56] Perhaps, we might correctly state that this problem has not yet been finally elucidated. We can neglect the variation in the effect of the intrinsic absorption of molecules when the spectra are excited in a region where the substance is transparent. As the frequency of the exciting line approaches the absorption band, this factor begins to be significant, and finally becomes decisive. Here also the exact form of the functional relationship is not clear enough. Some information on this problem can be found in [57-60,56].

Colored substances occupy a special place in Raman spectroscopy. They involve problems of excitation

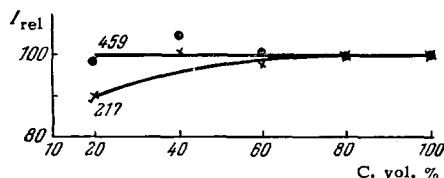


FIG. 6. The relation of the molar integral intensity coefficients of the 459 and 217 cm^{-1} bands of carbon tetrachloride to its volume concentration in mixtures with 1,2-dichloroethane. The refractive indices of the components of the mixture are approximately equal, but the dielectric constants differ considerably (2.24 and 10 for carbon tetrachloride and 1,2-dichloroethane, respectively).

sources and emission detectors which will be taken up later. It is appropriate here to touch on the problem of three methods of taking into account the self-absorption of these substances.

One of the methods, developed in [61-67], is based on a theoretical analysis of the conditions of passage of light through the cuvette containing the colored substance. An idealized illumination geometry is considered, and it is assumed that the Lambert-Beer law is strictly obeyed. For substances that do not absorb very strongly, the theoretical and experimental data agree in most cases within the limits of possible experimental errors. However, it is dubious that the simplifying assumptions are well-grounded in the region of strong absorption. The correct way to take into account total reflection within the cuvette is also a difficult topic for the theoretical analysis of the problem.

Another method is purely empirical. It consists in constructing a family of curves, which separately take into account the absorption of the exciting and the scattered radiation. [54-56] A new calibration is required for each apparatus. This is a defect of this method. However, its unquestionable advantage consists in the possibility of applying it to any system. Thus it seems that we should favor it in those cases when we require exact information on the band intensities. One can combine the theoretical and empirical methods. [42,25,60]

In the third method, one uses an internal standard, or a substance having suitable Raman bands, relative to which one can perform the intensity measurements. The scales based on the use of carbon tetrachloride and cyclohexane are widely applied. However, it is more convenient in many cases to refer the intensities to the 1710 cm^{-1} band in the acetone spectrum. [68-70] The point is that acetone is a rather universal solvent, and its band at 1710 cm^{-1} is situated in the same part of the spectrum as many of the bands that are commonly of great interest (the vibrations of the nitro- and nitroso-groups, the benzene and other rings, and the C=C, C=N, and N=N double bonds). This fact ensures that the self-absorption of the light will be taken into account more accurately.

In conclusion, we shall remark on the choice of units for fixing the concentrations of substances. In comparing the intensities of bands belonging to the spectra of different molecules, it would be more correct to express the concentration in terms of individual molecules. In this way, we can take into account the factor of the density of the substance. We can make an exception only for highly dilute solutions, e.g., in studying resonance spectra. In these cases we can use molar concentrations.

Conclusions. It is a difficult problem to obtain correlative intensity values in Raman spectra, owing to the influence on the measured quantities of various factors determined by the geometry of illumination, as

well as by other characteristics of the apparatus and the properties of the substance itself (optical effects, intermolecular interactions). Only the illumination geometry is amenable to theoretical analysis. The overall influence of the optical effects must be estimated experimentally. As an approximate criterion for them, we can use the behavior of the totally-symmetric vibration in the spectrum of carbon tetrachloride, which, as experiments have shown, is not very sensitive to intermolecular interaction.

D. The Effect of the Refractive Index of the Liquid on the Depolarization of the Bands

Equation (12), which was cited above, giving the relation of the depolarization to the divergence of the beam of exciting light, can be written more conveniently in another form:

$$\rho'_0 = K (\rho_{\pi/2} \cos^2 \bar{\theta} + \sin^2 \bar{\theta}), \quad (21)$$

where $\bar{\theta}$ is the effective angle of incidence of the beam. Strictly speaking, the true illumination geometry must take into account also the refraction of the rays at the liquid interface. To do this, it suffices to use Snell's law. Koningstein and Bernstein^[71] have proposed an appropriate formula. It has the following form:

$$\rho'_0 = K \rho_{\pi/2} \left(1 - \frac{\sin^2 \theta}{n^2} \right) + K \frac{\sin^2 \theta}{n^2}. \quad (22)$$

Since the relation holds that $\sin^2 \bar{\theta}/n^2 \ll 1$ (for $n = 1.46$ —carbon tetrachloride; in the apparatus of the authors of^[71] this quantity is ~ 0.14), we should expect n to exert a substantial effect only on strongly polarized bands. With the current accuracy of measurements, considerably depolarized bands need no correction of this type.

4. PHOTOGRAPHIC AND PHOTOELECTRIC APPARATUS

At present, the photoelectric technique of recording Raman spectra has been very widely applied, in line with the advantages of this method in the measurement of band intensities in spectra. However, the solution of a number of problems amounts to determining as exactly as possible the positions of bands and lines. For instance, we encounter such problems in high-resolution spectroscopy of gases. In other cases we meet with difficulties depending on the properties of the radiation detector. In particular, this is the situation in the study of spectra of highly colored substances and spectra excited by the ruby laser. All of this has thus far required the use of photographic recording. Thus it is convenient to start this section with a brief characterization of some typical spectrographs.

A. Spectrographs

Welsh et al^[72] have described an instrument that

has been successfully applied to study gases. This is an autocollimating (Littrow) two-prism glass spectrograph having two interchangeable cameras. The larger of these has a relative aperture of 1:42. It corresponds to a dispersion of $2 \text{ \AA}/\text{mm}$ in the region about the 4358 \AA line. The prisms of the spectrograph are enclosed in a hermetically-sealed chamber furnished with thick glass windows of optical quality and surface preparation. A constant pressure is maintained in the chamber. Thus the dispersion of the instrument does not depend on fluctuations in the atmospheric pressure. All the optical surfaces (including even the windows of the prism chamber) are coated. The spectrograph is located in a thermostated chamber in which the temperature is maintained constant to an accuracy of $\pm 0.2^\circ\text{C}$.

In solving the same problem, Stoicheff^[73] took the course of building a high-resolution instrument using a diffraction grating. The instrument that he described was built about a 21-foot concave grating operating in an Eagle mounting. The grating has a ruled area of 7×3 in with 1500 lines/inch, and is capable of directing an appreciable fraction of the energy into the region around 5000 \AA of the second-order spectrum. The linear dispersion of the spectrograph is approximately $1.3 \text{ \AA}/\text{mm}$, and the optimum resolution 0.3 cm^{-1} .

Stammreich et al.^[74] were able to attain just as high a resolution, but in the region of 8000 \AA . They built a spectrograph having five interchangeable cameras, the longest of which had a focal distance of 840 mm and a relative aperture of 1:13. Using this spectrograph with excitation by the helium line at 5876 \AA , they studied^[74,75] liquid chlorine and interhalogen compounds. In particular, the spectrum of the former exhibited a fine structure in the bands, which, in the authors' opinion, is to be explained by the isotopic composition of the substance.

Gerasimova and Yakovleva have built three spectrographs of great relative aperture, having diffraction gratings and lens optics. These permitted them to conduct studies of extremely weak emissions at relatively high resolution.^[76] One of the instruments (SP-48) was designed for photography of separate regions (as much as 1000 \AA) in the visible. It has a camera with a focal distance of 70 mm, a relative aperture of 1:0.8, and is furnished with a grating with a ruled area of $136 \times 90 \text{ mm}^2$, with 1200 lines/mm. The spectrum is photographed on 16 mm film. The dispersion of the instrument amounts to about $100 \text{ \AA}/\text{mm}$, and the resolution to 3 \AA . The other spectrographs of this series are designed for the near ultraviolet and infrared. The last of these (SP-50) is of especial interest for Raman spectroscopy. Its working range is 8000 — 11000 \AA . The focal distance of the camera is 135 mm, and its relative aperture is 1:1.5. The grating has a ruled area of $121 \times 90 \text{ mm}^2$ with 600 lines/mm, and operates in the first order of the spectrum. The dispersion of the instrument is about the same as for the

SP-48, but the resolving power is lower (about 5 \AA).

Among the foreign commercially-produced instruments for Raman scattering, the one most often used is the Hilger E-612 spectrograph;^[77] a two-prism instrument having two interchangeable cameras of apertures 1:1.5 and 1:5.7. Its dispersion amounts to 64 and 16 \AA/mm , respectively, in the region of $\lambda = 4358 \text{ \AA}$. In the photoelectric variant, the instrument can be used as a monochromator. To do this, one collimating mirror is set up in place of the camera, and another off-axis mirror is set up to deflect the light beam to the side. Thus, the light passes twice through both prisms, and thereby the dispersion of the instrument is enhanced (6.7 \AA/mm in the same spectral region).

The industry in our country produces a series of instruments especially intended or suitable for studying Raman spectra. The most widespread in use is the instrument ISP-51.^[78,79] It is a three-prism glass spectrograph having two interchangeable cameras ($F = 120$ and 270 mm), covering the range $3600-10000 \text{ \AA}$; in addition, one can use in the instrument two other separately-supplied long-focus cameras ($F = 800$ and 1300 mm) or exit collimators having a photoelectric attachment.

Another spectrograph-monochromator, DFS-4, is constructed about interchangeable plane diffraction gratings having 600 and 1200 lines/mm, and mirror optics. Depending on the grating used, its dispersion is 13.5 or 6.5 \AA/mm , while its relative aperture is 1:7.3 or 1:10.4, respectively. The region of the spectrum is photographed on a flat film or plate.^[79]

The ISP-67 spectrograph is suitable for photographic study of spectra at especially high dispersion and resolution. It is furnished with three large glass prisms of 150 mm base. Each instrument can operate in two variants of the optical system: with a simple or an autocollimated ray path. There are three cameras with their corresponding collimators. The focal length of the long camera (calculated only for the autocollimating variant) is three meters. This makes possible a resolution greater than 200,000, whereby one can easily resolve lines 0.04 \AA apart in the region of 4000 \AA at a dispersion of 0.88 \AA/mm .^[79]

B. Spectrometers

The first experiments on photoelectric recording of Raman spectra began more than fifty years ago. In subsequent years, this method has been developed very intensively and perfected. Many instruments have been described in detail. We cannot and need not give an account of the problem in chronological order. The pertinent material is to be found in the review^[80]. It seems expedient here, in taking up the most recent advances along this line, to focus attention only on the results that the author finds most essential.

Specific requirements are imposed on the monochromator, which is one of the important parts of a

photoelectric apparatus; they arise from the characteristics of the photoelectric detector, which reacts to the light flux rather than the light intensity, in distinction from a photographic plate. Naturally, the parameters of the monochromator must ensure as high as possible a value of this quantity in particular, the light flux. The usually-applied criterion of "transmission of the instrument," which characterizes the light intensity in the focal plane, and is determined by the relative aperture of the camera, acquires a new meaning: "the transmission of the instrument in terms of light flux." Hence, we mean by a monochromator of high transmission in a photoelectric apparatus one that has a large diameter of acting aperture and the maximum permissible angular dimensions of the entrance and exit slits.^[29] The modern monochromators used in Raman spectroscopy are precisely of this type.

Since we are concerned with spectroscopic instruments, perhaps the most essential advance in recent years consists in the application of double monochromatization of the light. A commercially-produced apparatus of this type has been designed and built simultaneously in our country (DFS-12) and in the United States (Cary Model 81).

The prototype of the double monochromator produced in our country is a model of the instrument designed by Kiselev.^[81] This instrument is constructed according to the symmetrical double system of Ebert and Fastie (Fig. 7). Two flat gratings are set up on a common rotating stage, thereby simply and reliably solving the problem of correlating their motion. Since the dispersions of the two gratings in the adopted system are additive, the angular dispersion of the instrument is doubled. This compensates partially or completely for the light losses from the additional reflections. In the DFS-12 monochromator gratings are used of dimensions $150 \times 140 \text{ mm}$, with 1200 and 600 lines/mm, operating in the first or second order of the spectrum, respectively. The parabolic mirrors have a focal distance of 800 mm and a relative aperture of 1:5.3. The linear dispersion at the exit slit is 5.2 \AA/mm . The length of the slits is 40 mm. By a suitable adjustment of their curvature, the half-width of the slit function of the DFS-12 could be reduced to several tenths of a cm^{-1} .* The FEU-17 serves as the radiation receiver, while a direct-current amplifier is used for amplification. The spectra are recorded by means of a potentiometer with a pen on a paper strip.^[82] The detector-amplifier section in the photoelectric attachment to the instruments ISP-51 and DFS-4 is the same in principle.

Insofar as we know, there is no systematic description of the Cary Model 81 spectrometric apparatus in

*In photoelectric recording, the size of the signal at fixed resolution is proportional to the angular dispersion of the spectroscopic instrument.^[29] Hence it is always more advantageous to work with the higher orders of the grating.

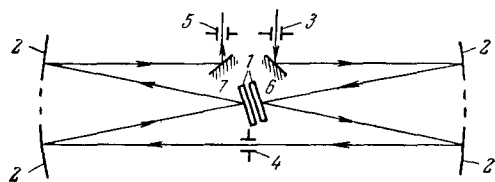


FIG. 7. Diagram of the double monochromator of Kiselev. 1 - Diffraction gratings; 2 - spherical mirrors; 3, 4, 5 - entrance, intermediate, and exit slits; 6, 7 - collimating mirrors.^[81]

the literature. However, we can put together an idea of this apparatus from fragmentary information in a series of publications.^[83-85]

Figure 8 shows a diagram of the Cary Model 81 apparatus. A component part of it is a double, two-slit monochromator having flat diffraction gratings arranged in the Shurcliff system.^[86] The gratings have a ruled area of 100×100 mm, with 660 lines/mm, and are able to concentrate a considerable part of the energy into the first order of the spectrum at 4500 \AA . * When one uses the two-slit variant of the instrument, a parasite line appears in the spectrum near the 4358 \AA mercury line at a distance of 120 cm^{-1} . The collimators are spherical off-axis mirrors. The slits are 100 mm long. A special image-slicer is used to illuminate them, transforming the rectangular aperture of the cuvette into 20 narrow images. The capacity of the usual cuvette is 4.5 cm^3 , but with this apparatus one can also study considerably smaller quantities of liquid, as low as 0.05 cm^3 . The spectra are excited with a helical low-pressure mercury lamp. The radiation detector consists of two photomultipliers. A rotating mirror directs the scattered light and the direct light of the lamp alternately into the one or the other photomultiplier. In addition, the signals are integrated. The electrical system permits one to record the ratio of the useful to the reference signal, thus taking into account fluctuations in the brilliance of the excitation source. It has been stated that the instrument has a resolution of 10 cm^{-1} , and reproduces bands in intensity to an accuracy as great as $\pm 0.2\%$.^[83] On the other hand, judging from the data of ^[25], the half-width of the slit function for the double-slit variant is no greater than 2.3 cm^{-1} .

As is known, double-beam instruments are widely used in infrared spectroscopy. In particular, their significance consists in eliminating the bands of the solvent from the observed spectrum. This is achieved by electronic means. Analogous problems can also arise in the study of Raman spectra of two-component mixtures. To solve them, Zubov, Petrash, and Sushchinskiĭ^[87] have developed and described a suitable apparatus. Here the light fluxes scattered by two different cuvettes containing liquid are alternately directed into the spectroscopic apparatus by a rotating

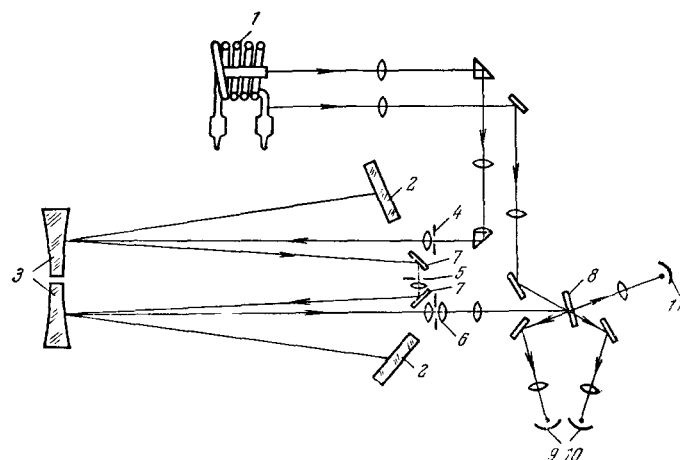


FIG. 8. Diagram of the Cary Model 81 apparatus. 1 - Illuminator; 2 - diffraction gratings; 3 - spherical off-axis mirrors; 4, 5, 6 - entrance, intermediate, and exit slits; 7 - collimating mirrors; 8 - rotating mirror; 9, 10, 11 - photomultipliers.^[83]

mirror. If the intensity of both of the light beams is the same, the resultant photocurrent at the photomultiplier output will be unmodulated, and hence will not be passed by a selective alternating-current amplifier. The situation differs when the intensities of the beams are unequal: here the resultant photocurrent contains an alternating component that can be recorded by the system. Thus, the apparatus permits us to determine the difference between the two signals. To illustrate the possibilities of such an apparatus, Figs. 9-11 show a series of spectra taken from a paper by Pivovarov and Levin.^[88]

The application of the photoelectric technique of recording in Raman spectroscopy has mainly arisen from the attempt to improve the accuracy of intensity meas-

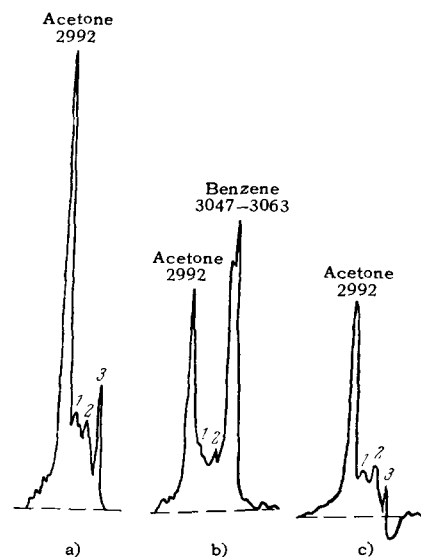


FIG. 9. The separation of the partially overlapping bands in the Raman spectrum of an acetone-benzene mixture using a difference system. a) Spectrum of acetone; b) spectrum of the mixture after compensation for the benzene band.^[88]

*Private communication from P.A. Bazhulin and Kh. E. Sterin.

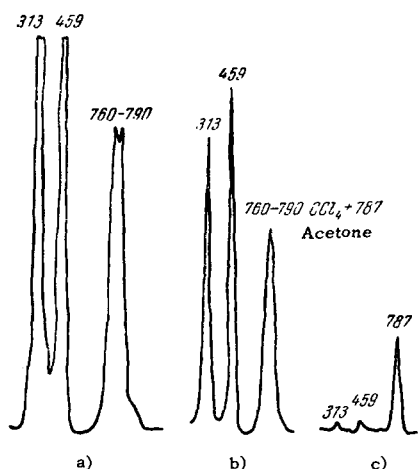


FIG. 10. The separation of the completely overlapping bands in the Raman spectrum of an acetone-carbon tetrachloride mixture using a difference system. a) Spectrum of carbon tetrachloride; b) spectrum of the mixture; c) spectrum of the mixture after compensation for the carbon tetrachloride band.^[88]

urement. The material presented above shows that this problem has been solved. However, at the same time the conditions for determining the band frequencies have deteriorated considerably. A situation has arisen in which one cannot effectively use the high resolving power of certain photoelectric instruments such as the DFS-12.

The way out consists in making fiducial marks on the frequency scale on the paper chart while recording the spectrum. For example, in the DFS-12 instrument, such marks are made every 100 cm^{-1} . Linear interpolation within this interval ensures an accuracy of only $1-2 \text{ cm}^{-1}$, which is insufficient in a number of cases. The problem has been solved ingeniously in connection with a device for making considerably more frequent marks in a study by Abramson, Kononov, Mogilevskii, Murzin, and Slavnyi.^[89] To do this they used a Fabry-Perot etalon having a spacing between interference fringes of 5 cm^{-1} . The light from the etalon filled part of the entrance slit of the monochromator. The interference pattern was recorded by a separate photomultiplier. Its output signal controls the recording of the spectrum. In the authors' opinion, the error in determining the distance between reference points is no greater than 0.25 cm^{-1} , which characterizes the accuracy of frequency measurement. Thus, the latter quantity has been brought into agreement with the attainable resolution in the spectra.

C. Sources for Excitation of Spectra

1. Mercury lamps. More than ten years ago, new excitation sources began to be used in Raman spectroscopy: powerful low-pressure mercury lamps of the Toronto type.^[90] Their distinguishing feature consists in local water cooling of the liquid mercury elec-

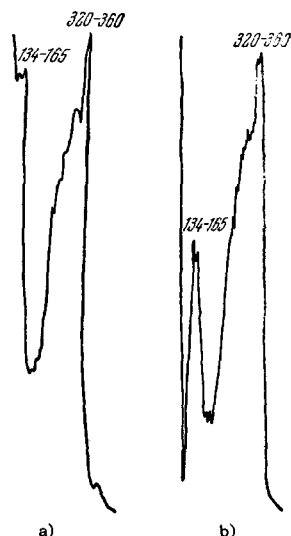


FIG. 11. The Raman spectrum of a solution of SbCl_3 molecules, as obtained: a) with an ordinary system; b) with a difference system. In the latter case, the background is subtracted from the tail of the exciting line $\lambda = 4358 \text{ \AA}$.

trodes, thus attaining a low vapor pressure together with a great discharge power. Possessing a favorable composition of the radiation, fine lines and low background, they displaced from use the high-pressure mercury lamps, and became an irreplaceable part of the modern spectroscopic apparatus. In recent years, Toronto-type lamps have begun to be produced in our country.

The lamps made in our country are intended for operation in a horizontal position. They are built of Pyrex, and are helices having an inner diameter about 80 mm and consisting of 3 or 5 turns. Both electrodes are liquid mercury. Starting of the lamp requires voltage pulses from a high-frequency generator. A certain amount of a noble gas (helium) is introduced into the lamp to facilitate starting. This measure eliminates the necessity of preliminary heating of the mercury and of having an auxiliary electrode. As the measurements of Sosinskiĭ^[91] have shown, when the amount of the gas present is favorable, its lines in the spectrum are very weak, and do not interfere in the study. The discharge current of the lamp and the voltage drop across its terminals are within the ranges 8-12 A and 80-90 V, respectively. The lamp is mounted in an illuminator having all the necessary motions and ventilated with a fan.

In spite of their high quality of spectrum, low-pressure mercury lamps are still being improved in a number of respects. Here the most important factor consists in having independent water cooling of the working section, so as to increase the power and to narrow the lines further, and in providing them with the most advantageous and convenient shape for the solution of special problems.

Stoicheff is to be credited with priority in the former line of improvement (^[73]; see also the review ^[3]).

Subsequently, the idea of supplementary cooling has been extended to lamps of various shapes.^[72,92-96] Various means of construction in building them have been proposed.

Certain authors, e.g.,^[95], prefer internal cooling. This is achieved by passing running water through a specially sealed-in inner tube. It has been possible to do this even with a helical lamp.^[72] In other lamps, cooling is brought about by an outer jacket sealed to the discharge bulb,^[73] or joined to it with rubber tubes.^[96] Finally, helical lamps have also been built in which the working section is enclosed in a hermetically-sealed cavity containing running water.^[97,98]

Apparently, a lamp of the latter type has been developed by the company Quarzlampen Gesellschaft (Hanau, West Germany).^[97] The lamp is designed to operate in a horizontal position, and is made in two variants: of quartz and of glass of a special composition that does not darken on prolonged use. The latter is very important in view of its increased power. The cavity through which the running water circulates is sealed with the aid of two quartz cylinders on gaskets. The lamp has four turns with an inner diameter of 60 mm. High-frequency pulses are used to start the lamp. Starting is facilitated by an auxiliary electrode and by preliminary heating of the mercury. The working current is as great as 20 A, and the power consumption is 1.5 kW. A suitable hermetically-sealed jacket eliminates the harmful effect of the scattered radiation, which is especially marked in the quartz variant of the lamp. A lamp of analogous design described by Chisler^[98] has a considerably higher power (6 kW).

The relation of the efficiency of a source to its shape is quite obvious. Thus, for the same brilliance of emission and for a given length of working cuvette, a helical lamp is unconditionally more advantageous than a straight lamp. Even better is a lamp providing continuous emission from a cylindrical cavity. A source of this type was first built in a study by Pliva, Schneider, Stokr, and Ulbert.^[99] It was intended to operate in a vertical position. Later, Kondilenko and Vorob'eva^[100] described a horizontal lamp of a similar type, the technology of its construction, and some test results.

The horizontal lamp consists of two coaxial cylinders sealed together, of diameters 30 and 70 mm. Tubes for liquid-mercury electrodes are sealed to the outer one. Without high-frequency pulses, the lamp is started with preliminary heating with the aid of an auxiliary anode. The length of the working part of the lamp is 200 mm, while the current used can be as high as 25 A. A good spectrum of carbon tetrachloride can be obtained with this source on the ISP-51 instrument with a small camera in 15 seconds. When mixed with benzene, carbon tetrachloride can be identified at a concentration of 0.07%.

The advantage of these lamps consists not only in

their shape. Apparently, the latter affects the nature of the discharge favorably. This is evidenced by the fact that the light output shows a much more marked dependence than usual on the value of the discharge current.^[72,94,100] Consequently, the optimum conditions of use of lamps with continuous emission from a cylindrical cavity is shifted toward greater discharge currents. This is an additional source of their efficiency. A further increase in their power can probably be attained through independent water cooling of the working section. In actuality, its design would encounter great technical difficulties.

In one respect, lamps having continuous emission from a cylindrical cavity are still inferior to helical lamps: their inner-cylinder diameters are small. This practically rules out using them in low-temperature studies. However, even in an ordinary experiment, this gives rise to certain difficulties, e.g., in the choice of light filters. Therefore, the further improvement of these lamps must, in particular, consist in enlarging their dimensions.

In a number of cases, one requires sources of special shapes. We shall discuss in the next section some examples of this sort relating to the study of powdered substances. Particularly for this reason, Moser and Stieler^[101] constructed a U-shaped lamp with a side window permitting the focusing of the light on the powdered sample with the aid of a high-aperture condenser. To increase the current density, the horizontal section of the lamp has a jacket with independent water cooling. Owing to these measures, the nature of the discharge is maintained, but its brilliance increases markedly. Figure 12 shows a sketch of the lamp. Recently Geppert and Scholz^[102] have built another such lamp. They also studied its spectral characteristics.

All of the above-described lamps are supplied by direct current. The usual power supply consists of a high-power stabilizer and a rectifier. This is a very cumbersome setup. An alternating-current lamp is more convenient to use. Bridoux and Delhaye^[103] have built such a source. It has four liquid mercury electrodes: one air-cooled cathode and three water-

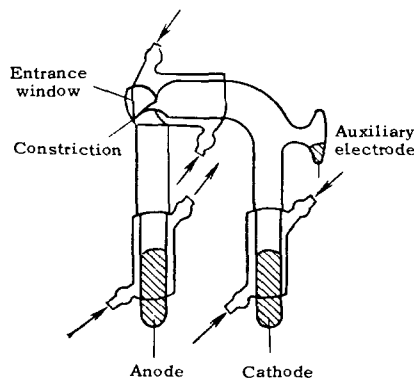


FIG. 12. Diagram of a "point-source" low-pressure mercury lamp.^[101]

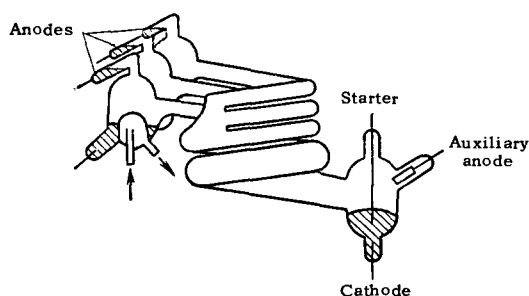


FIG. 13. Diagram of an alternating-current low-pressure mercury lamp.^[103]

cooled anodes (Fig. 13). Its spectroscopic characteristics are the same as those of an ordinary lamp of the Toronto type.

2. The problem of studying colored substances — lamps in which the discharge takes place in noble gases and in alkali-metal vapors. However the mercury lamp may become perfected, we still cannot consider it to be a universal excitation source for Raman spectra. It often becomes necessary to study highly colored substances. For example, these include a vast class of molecules from organic chemistry containing alternating single and multiple bonds and chromophoric groups. Such molecules are of great interest in theoretical and practical respects. The development of a method of studying colored substances amounts to the construction of a source having exciting lines shifted into the orange-red region. There are no suitable lines for this purpose in the mercury spectrum (the yellow doublet at 5770–5790 Å is very weak, and Raman lines excited by it are doubled). This fact has led certain researchers to concern themselves with the design of special sources.

The first studies along this line were conducted several decades ago by Wood, Krishnamurti, and Thompson.^[104] However, this new technique has undergone considerable development in recent years. Above all, this is due to the studies of Stammreich^[105] and Delhaye.^[106]

In solving the problem, Stammreich first took the course of building gas-filled lamps. In 1956 he developed and described high-voltage glow discharge lamps filled with helium, neon, argon, krypton, and xenon. The spectra of these gases contain a rich selection of lines situated in the long-wavelength region, including the near infrared. Certain of them are sufficiently intense, and can be used as exciting lines. All the lamps were made of glass tubing of 5 mm diameter wound in a helix having an uncoiled length of about a meter. When a voltage of 1200–2000 V was applied, the working current of a lamp amounted to 500 μA. Using such sources, he could obtain spectra of a multitude of previously unstudied molecules. A resume of all the results is found in ^[107].

The problem of studying the Raman spectra of colored substances is not completely worked out by the

construction of gas-filled glow-discharge lamps. Experience has shown that these lamps are distinguished by a number of faults. The major ones consist in the lack of stability of the light and electrical parameters. In some cases the lamps produce inductive interference thereby ruling out (or in any case hindering) the use of the photoelectric technique of measuring the spectra. Even the high supply voltage of the lamps in itself complicates the conditions of using them. Thus certain authors tend to use low-voltage arc-discharge sources.^[106,107]

We can judge as to the characteristics of these latter sources from the description by Kir'yanova, Pivovarov, and Yakovlev.^[108a] The lamp that they built is linear in shape, and is made of glass tubing of diameter 40 mm and length 120 mm. The electrodes, which are oxidized coils designed for high current strength, are contained in thickened bulbs sealed on at an angle. The lamp is filled with helium at a pressure of 2 mm Hg. Here the starting potential does not exceed 170 V, and the discharge is quite stable. The working current is 8 A, and the potential drop is 100 V. After 200 hours, such a lamp continues to burn stably without any appreciable signs of darkening of the glass. To illustrate the operation of the low-voltage lamp, Figs. 14–16 show some spectra. They were recorded with the photoelectric apparatus described in ^[108b]. As we see, spectra can be excited not only with the intense 5876 Å line, but also with the considerably weaker helium lines at 4471 and 5016 Å. The latter point is essential in a number of cases, e.g., in studying the frequency characteristics of the scattered radiation.

Raman spectra in the long-wavelength region can also be excited with lamps in which the discharge takes place in alkali-metal vapors. Here it is advantageous to use the resonance lines: they are intense and can be selectively absorbed in the beam of scattered light. The resonance doublets of cesium (8521 and 8943 Å) and rubidium (7800 and 7948 Å) are especially suitable. The above-cited study of Stammreich^[105] describes the results of the first experiments with the cesium and rubidium lamps. King and Lippincott,^[109] as well as Miller, Carlson, and White,^[110] have been able to

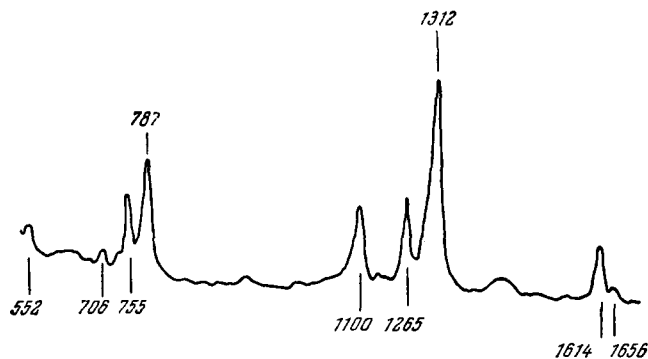


FIG. 14. Raman spectra of *p*-dimethylaminonitrostyrene molecules. Exciting line: $\lambda = 5875$ Å (helium).

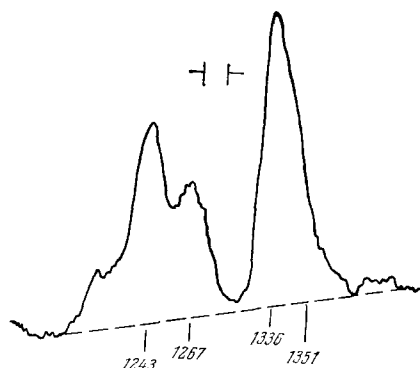


FIG. 15. A portion of the Raman spectrum of o-nitroaniline molecules. Exciting line: $\lambda = 5876 \text{ \AA}$ (helium).

obtain the spectra of certain molecules using commercially-available sodium lamps. Owing to the closeness of the components in the sodium resonance doublet, all the Raman lines proved to be doubled. One of the difficulties in constructing alkali-metal vapor lamps apparently involves their chemical reactivity.

The amalgam lamps described by Ablekov, Zaitsev, and Pesin^[111] are of great interest; the authors developed them to study the fine structure of the Rayleigh line. They are constructed just like the low-pressure lamps, except that their electrode sections are filled with a liquid amalgam of zinc or cadmium instead of pure mercury. Evidently, one can use the amalgams of other metals as well. The emission lines of the metals added to the mercury prove to be very narrow and intense. The latter fact, as the authors of^[112] assume, involves the phenomenon of optical amplification (induced emission). Undoubtedly, experiments to apply these lamps to excite Raman spectra would be worthwhile.

3. Power supply of lamps by a microwave generator.

A series of publications in recent years has been concerned with a new method of power supply of lamps. It is based on the use of the electromagnetic field of microwave^[106,113] and radiofrequency generators.^[114] Here one no longer requires electrodes. The lamps are extremely simplified. The nature of the discharge remains favorable. The new method is suitable for power supply of both gas-filled lamps of any configuration and lamps containing the vapors of various metals. Certain limitations are imposed on the dimensions of the lamps alone. Good results have been obtained with these lamps. We shall give some examples. Ham and Welsh^[113] describe helium, sodium, and mercury electrodeless lamps supplied by a microwave generator. They are made in the form of a Dewar flask. The cuvette volume is 2 ml. An intense spectrum of the CCl_4 molecule is obtained in 2 min (exciting lines: $\lambda = 4358 \text{ \AA}$, and the components of the sodium doublet at $\lambda = 5889\text{--}5895 \text{ \AA}$). It was possible to excite the spectrum of the previously unstudied molecule S_2Cl_2 with the helium line at $\lambda = 5876 \text{ \AA}$. Analogous lamps filled

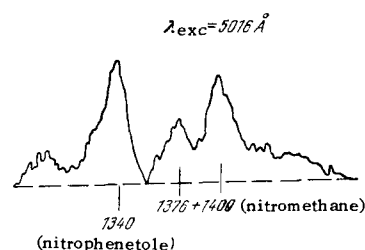
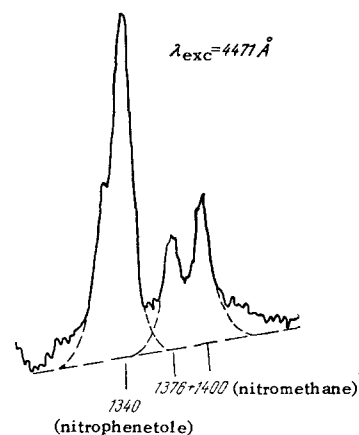


FIG. 16. A portion of the Raman spectrum of p-nitrophenetole molecules excited by the lines $\lambda = 4471$ and 5016 \AA of helium (solvent = nitromethane).

with potassium and rubidium vapors permitted the same authors to photograph the spectrum of liquid bromine in 15 minutes.^[113] In^[115], an electrodeless helium lamp was used to study the TiBr_4 molecule, whose spectrum had not been known.

4. The pulse technique of exciting spectra. Experiments on pulsed power supply to lamps occupy an important place in the development of new technical means of studying Raman spectra. These were carried out by Delhaye^[116] and by Delhaye and Delhaye-Buisset.^[117] For this purpose, the authors built a mercury lamp fully analogous with that described by Pliva et al.^[99] The lamp was supplied from a battery of condensers of capacity 12–24 microfarads, charged to 4000 V. Energies up to 200 joules were released in each pulse. The average power of the lamp amounted to 5 kW. They also used a hollow electrodeless lamp supplied from a microwave generator. The radiation was received by a photomultiplier. The resulting electric signal was applied to an oscillograph. For resolution of the light, a high-aperture prism apparatus was used. With the apparatus that they developed, they could record the spectra of a number of substances at a maximum scanning rate as great as about 20,000 $\text{cm}^{-1}/\text{min}$. Delhaye attained a further increase in the rate (to 60,000 $\text{cm}^{-1}/\text{min}$) by increasing the power of the lamp and using an improved spectroscopic apparatus.^[118]

The initial problem of the authors consisted in the spectroscopic study of the kinetics of chemical reac-

tions. However, the development of the pulse technique has also a broader significance. Pulsed supply permits one to improve the signal-noise ratio by electronic means, and thus to increase the threshold sensitivity of the photoelectric apparatus.^[119,120] Increasing the power of the lamp acts in the same way. Actually, here the problem of spectral line width (and also the intensity of the continuous background) under the conditions of the powerful pulse discharge remains insufficiently clear, and requires additional study. Without question, the pulse technique is worthy of further development.

5. The use of the laser to excite spectra. As we know, lasers, for which varied applications are being found, are being very intensively developed at present. In particular, experiments have been described on the use of the laser to excite Raman spectra.^[121]

In ^[121], the laser was made from a ruby rod containing 0.05% chromium. The ends of the rod were worked to an accuracy of 0.2 fringes and coated, one of them with an opaque silver film, and the other with a semitransparent one. To stabilize the frequency of the emerging radiation, the rod was cooled in nitrogen gas chilled with liquid nitrogen. As usual, the optical pumping was carried out with a xenon lamp. The laser operated at a frequency of three flashes per minute. The energy of each flash amounted to about 3000 joules, and the duration was about one millisecond. The spectra were obtained with from one to a hundred flashes.

The slightly diverging beam at the exit of the rod was directed with a condensing lens onto the cuvette containing the liquid. In order to increase the efficiency, a considerable portion of the cuvette was coated on the outside with barium sulfate. The spectra were recorded by the photographic method. A high-aperture spectrograph was used. A multitude of parasite lines was observed in the initially obtained spectra. Part of them were due to the entrance into the instrument of the fluorescent emission of the ruby, and others to the emission of the xenon lamp. The elimination of the parasite lines was achieved by separating the rod and the cuvette considerably. This is made possible by the small aperture of the exciting light. The authors show Raman spectra of benzene and carbon tetrachloride, free from parasite lines, and obtained with a distance of 1.5 meters between the rod and the cuvette.

In other experiments,^[122] a system was used in which the semitransparent mirror was displaced outward. The cuvette containing the liquid was placed between the rod and this mirror, and thus the authors of ^[122] were able to discover a new phenomenon under giant-pulse conditions: stimulated (coherent) Raman scattering. It turned out that only certain vibrations are relatively easily generated in the spectra of benzene, nitrobenzene, toluene, 1-bromonaphthalene, pyridine, cyclohexane, and deuterated benzene. Carbon tetrachloride and sulfuric acid were completely inactive, while water, acetone, and ortho-dichlorobenzene

were weakly active. The significance of the results obtained extends far beyond the limits of mere refinement of the technique of exciting spectra. These experiments have opened up a new field of Raman spectroscopy, very important in theoretical and applied respects. Intensive work is being continued along this line.^[123-127]

Conclusions

At present, experimenters have at their disposal photographic and photoelectric apparatus for recording Raman spectra that permit one to make precision measurements at high resolution, and also various sources for exciting spectra that are suitable for working over a very broad spectral range, and in particular, in the near infrared. The problem has thereby been solved of studying highly colored substances of importance in applied and theoretical chemistry. Various means of power supply of the lamps have been successfully developed. Especial attention is to be paid to the pulse technique of power supply of lamps, which permits one to increase the threshold sensitivity of the Raman-scattering method, as well as to study fast processes spectroscopically. Experiments have been described on application of a ruby laser as the source for exciting the spectra. Here an extremely important result was obtained: a new phenomenon was found of stimulated, coherent Raman scattering, which continues to be under intensive development.

5. SPECIAL METHODS

A. Powdered Substances

Many substances occur under ordinary conditions in the solid crystalline state. Sometimes they are difficultly soluble and decompose on melting, and hence cannot be studied either in solution or in the melt. On the other hand, in solving a number of problems one often has to compare the spectra of a substance in different states of aggregation. All of this makes it necessary to grow single crystals, which involves a great expenditure of time and is not always achievable or possible. Hence, the development of methods that permit one to obtain fully valid spectra from crystalline powders is a very important problem. Such methods should prove to be irreplaceable, at least in those cases when one does not need to know the polarization properties of the emission. More than thirty years have elapsed since the first experiments to study powders. However, considerable advances on this problem have been made only in the last decade. This section will be concerned with reviewing chiefly the most recent years.

One difficulty in obtaining Raman spectra from powders involves the marked enhancement of the mercury lines in the scattered radiation. While in the spectrum of a transparent liquid the exciting line in the Rayleigh

scattering exceeds the average Raman band in intensity by several hundred times,^[128,129] in the spectrum of powdered naphthalene this ratio is increased by approximately four orders of magnitude.* The light of this line is markedly increased, owing to reflections from the particles of the substance; and when it enters the spectroscopic apparatus, it is scattered by the optics, the mountings, and other internal parts. A continuous background is produced. According to the measurements of^[130], the intensity of the background can vary within the range of 10^{-3} – 10^{-4} of the intensity of the transmitted monochromatic light. Consequently, in this case the background from this source is stronger than an ordinary Raman band by a factor of no less than a thousand. It prevents our observing it.

Another difficulty in studying powders is due to the continuous background from the source itself. In high-pressure mercury lamps, its intensity in comparison with the blue line at $\lambda = 4358 \text{ \AA}$ amounts to 5×10^{-4} on the average.^[131,132] Since an ordinary Raman band of a powdered substance has a relative intensity of the order of magnitude of 10^{-6} – 10^{-7} in the same units, the background from the lamp also becomes a very serious obstacle to the experimenter.

However, even if in some way we can eliminate the above-mentioned difficulties, we must always consider the fact that a crystalline powder, which is as a rule a poorly-transparent medium, limits the depth of penetration of the exciting radiation, and thus the number of particles participating in the act of Raman scattering is limited. Hence, the spectra of powdered substances are often distinguished by relatively low intensity, and crystals that are too fine-grained are in many cases totally unsuitable objects for study.

Apart from the apparatus proposed as early as 1937 by the German school of spectroscopists,^[133] which was complicated to build and adjust and of low aperture, we can state that, within the limits of the photographic technique of recording, there is a single means, at least partial, of solving the problem of the spectra of powdered substances. It amounts to using supplementary light filters. One of these is placed in the illuminating beam of light, and the other in the scattered beam. Provided that the first filter isolates the exciting line, and the second one isolates a frequency range in which the most important Raman bands lie, the spectrum will prove to be considerably freed from the interfering radiation.

In most cases it is preferable to excite the spectrum with the mercury blue line at $\lambda = 4358 \text{ \AA}$. However, it is precisely in this region of the spectrum that there are no absorption filters with steep enough boundaries between transmission and absorption. Hence, in using the method involving these supplementary filters, in most cases one cannot obtain the bands in the spectra having relatively low frequencies (below ~ 300 – 400

cm^{-1}). In addition, the filter in the illuminating beam greatly weakens the exciting line, while the filter in the secondary beam distorts the intensity distribution of the scattered radiation. These constitute the major defects of the method.

Guber and Riggert are responsible for a certain refinement in the described method; in 1951 they proposed the use of interference filters in the incident and reflected light, instead of absorption filters.^[134] A diagram of the corresponding apparatus is shown in Fig. 17. Using it, they obtained encouraging results. The secondary filter proved especially effective. By using two secondary filters, the authors of^[135,136] could reduce the background in the spectra even further, though at the expense of a quite considerable increase in the exposure.

However, interference filters are distinguished by one defect as compared with absorption filters: they have to be illuminated by narrow beams of light. The aperture of the collimators in the spectroscopic instruments seldom exceeds 10° , and hence in general it satisfies the required condition. The problem is more serious with the light beam incident on the substance. The usual method of illuminating the sample proves inapplicable in this case. One has to use a "point" source, and project its image on the sample, with the filter placed between the condensing lenses. Guber and Riggert^[134] used a mercury lamp having a flat window at the end used for illumination. Very convenient lamps having an increased radiation density have been specially built for this purpose and described by Simon, Kriegsman and Steger,^[135] by Moser and Stieler,^[101] by Heinz and Simon,^[137] and also by Geppert and Scholz.^[102] Certain information on these sources is to be found in the previous section.

It is self-evident that the aperture condition sharply lowers the efficiency of excitation. However, Tobin^[138] has shown that one can use ordinary absorption filters in the illuminating light beam emitted by a low-pressure mercury lamp without harming the quality of the spectra. This opens up the possibility of using wide-aperture helical lamps. A calculation made by the authors of^[138] shows that one attains thus a more-than-tenfold increase in the light flux incident on the sample.

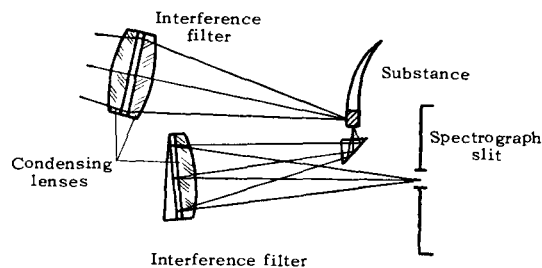


FIG. 17. Diagram of the excitation of Raman spectra of powdered substances using interference filters.^[134]

*Data of special experiments.

When one is interested only in the bands of frequencies in the range $700\text{--}1700\text{ cm}^{-1}$, it is reasonable to excite the spectrum with the green mercury line at $\lambda = 5461\text{ \AA}$, using absorption filters in the primary and secondary light beams. This involves the possibility of selecting a very good combination of filters. An efficient apparatus of this sort is described in [139]. Indeed, the use of a diffraction-grating spectrograph was required in its construction. Prism instruments are distinguished by very low dispersion in this region of the spectrum.

Up to now, we have been discussing various methods of exciting spectra of powdered substances using gas-discharge lamps. Danil'tseva, Zubov, Sushchinskiĭ, and Shuvalov [140] have obtained spectra from a number of powders excited by the 6943 \AA line of a ruby laser. The flash energy of the pumping lamp amounted to $1\text{--}1.8\text{ kJ}$. The crystal was cooled with the vapors of liquid nitrogen. In order to weaken stray radiation, the powdered sample was placed at a great distance (two meters) from the crystal. The spectra were photographed with a very high-aperture (1:1) spectrograph having a flat diffraction grating. They used Infra-760 photographic plates and Infrarapid-750 film. The slit width was $8\text{--}12\text{ cm}^{-1}$. The method of illuminating the sample was by transmission. From thirty to one hundred flashes were required to obtain the spectra. This indicates the relatively low efficiency of excitation.

It is clear from all that has been stated above that the excitation source is a very important element of the apparatus in obtaining Raman spectra from powdered substances. Previously, high-pressure mercury lamps had been used exclusively for this purpose. As has been noted, they are characterized by a high intensity of the continuous background, which considerably complicates the problem. A considerable effect was attained in [141,138,101] by the use of low-pressure lamps of the Toronto type, involving the low intensity of the background in these lamps, amounting to a value of the order of 10^{-6} .*

An important step in the development of methods of study of powdered substances was the application of photoelectric measurement of the spectra. This was first carried out in [141]. Subsequently, analogous publications have appeared. [101,142] Another advantage was added here to the usual ones of photoelectric recording over photographic: it became possible to adapt a double monochromator to obtain the spectra. When using a low-pressure mercury lamp, which is practically free from continuous background, double monochromatization of the light most radically eliminates parasitic scattering and the ghosts characteristic of the diffraction grating. Here it becomes possible to approach the exciting line itself, i.e., to obtain the complete spec-

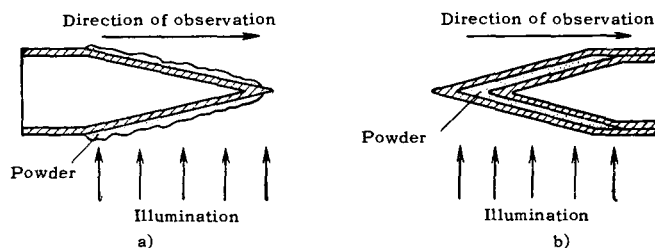


FIG. 18. Diagram of the excitation of Raman spectra by powdered substances in a conical cuvette. a) In reflected light; b) in transmission.

trum of frequencies, including the low ones, without distorting the intensities of the lines and bands. Another important fact is that with double monochromatization one can reduce the light losses to a minimum, or even compensate them totally by opening the slits, as is permitted by the sharply increased angular dispersion of the instrument. Consequently, this variant of the method of studying powders is effective in all respects. It was first proposed in [141] and carried into practice in [81]. Recently the Cary Model 81 spectroscopic instrument has been used for an analogous purpose. [142]

Irrespective of the method of recording the spectra, the problem always arises of the most rational method of illuminating powdered samples. Observations are often made in transmission by illuminating a planar cuvette of optimum thickness containing the powder with a wide-aperture condensing lens. [143-146] However, a conical cuvette containing the specimen, operating in transmission or reflection, proves much more effective (Fig. 18). The latter method is more advantageous also for the reason that in carrying it out, one does not require tedious experiments to establish the optimum thickness of the layer, for it is achieved automatically. A method of illuminating the sample proposed by Bergmann and Thimm [147,148] is very curious. It is based on using a cuvette having the form of an Ulbricht sphere, as shown in Fig. 19. Using such a cuvette, intense spectra of wet (turbid) benzene and powdered naphthalene could be photographed in eight minutes. In the authors' opinion, one can obtain thus new, important characteristics of the Raman spectra, namely, the quantum yields. In [149] and some subsequent studies, experiments were undertaken to obtain spectra from pressed tablets, in analogy to the corresponding technique used in infrared spectroscopy. The observation was made in transmission. The powders were pressed with KBr without a filler. It is as yet difficult to judge as to the effectiveness and advantages of this method over those described above.

The essential role of the dimensions of the scattering particles has been noted above. This problem has been the special topic of a series of studies. [150,151,142] For example, for those reputedly difficult substances, the inorganic crystals, which do not give sharp spec-

*Data of special experiments using a double monochromator. The value of 10^{-5} given in [132] is apparently too high, owing to parasitically scattered light.

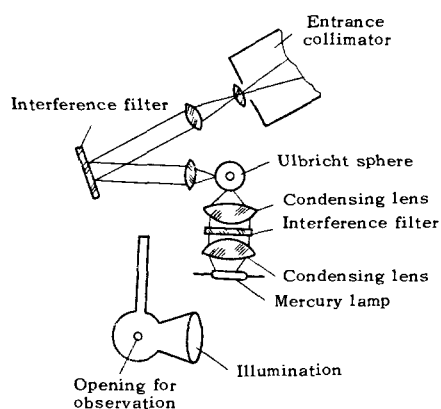


FIG. 19. Diagram of the excitation of Raman spectra of powdered substances in an Ulbricht sphere.^[147,148]

tra, the dispersity of the particles was varied from 1.5 to several hundredths of a millimeter.^[150] When the particle dimensions were less than 0.1 mm, in most cases spectra were not obtained, even with considerable exposures. However, obviously, the critical dimensions of the particles must depend both on the method of study (recording of the spectrum, sample illumination) and on the nature of the substance itself.

The solution of many problems, in particular those involving the determination of molecular structures, requires a knowledge of the intensity coefficients of the Raman bands. Hence, methods of determining these quantities acquire great importance in the spectra of powders as well. However, the performance of such measurements involves a specific difficulty: their results depend on the dimensions and packing of the particles, and also on the thickness of the effective layer of the substance. In order to obtain data that can be correlated, we might try to standardize the experimental conditions. However, this is difficult to achieve in practice. Besides, such a standardization would be of little avail in studying colored crystals, which require that we take into account the self-absorption of the exciting and scattered radiation within each particle.

It is better to seek a way out of the situation in using an internal standard. This is precisely what the authors of^[151] have done. They excited the spectrum in transmission with the mercury resonance line at $\lambda = 2537 \text{ \AA}$, and chose as an internal standard another mercury line situated in a suitable region. Thus they took into account the combined influence of all the factors enumerated above.

However, such a variant of the method is far from reproachless. First of all, it is not distinguished by universality. With another choice of exciting lines, e.g., with $\lambda_{exc} = 4358 \text{ \AA}$, one can no longer find standard lines in the spectrum of the source in suitable positions. This is especially important in studying highly colored powders. It is also clear, as we know, that it cannot be applied to measure spectra obtained in re-

flected light. However, it is precisely this variant of the method that merits preference by its convenience and simplicity.

Another variant of the method of measurement is free from these defects. Here the internal standard consists of suitable Raman bands of a specially added substance. The 1380 cm^{-1} band of naphthalene has been chosen as the internal standard in experiments of this sort.^[152] The powders being studied (various aromatic compounds) and naphthalene were ground in a mortar and carefully mixed to obtain as homogeneous a mixture as possible. An oblique section of a wooden cylinder was coated with a layer of it. The layer was illuminated by a helical low-pressure mercury lamp. The observation was made from the side.

If the powder being studied is transparent in the region of the exciting and scattered radiation, then quite obviously this method of determining the intensity coefficients should give correct results for a sufficiently homogeneous mixture of fine particles. When working with colored powders, a further condition must be satisfied: the exciting line must penetrate into the layer to a depth exceeding the dimensions of the particles several-fold (a depth estimated to be 0.05–0.1 mm). Only thus can we correctly take into account the self-absorption within the colored particles.

We can obtain indirect evidence on the relative depth of the effective layer of the powder in each individual case by studying the relation of the intensities of the Raman bands of the colored powder to its mole fraction in the mixture. Evidently, observation of a proportionality here would mean that the exciting radiation penetrates deeply enough into the layer, rather than being absorbed upon passage through even a single colored particle. This also will establish the limits of applicability of the method.

Figure 20 shows such a graph, referring to a mixture of p-nitrophenetole (a substance absorbing appreciably at the edge of the visible) and naphthalene. The

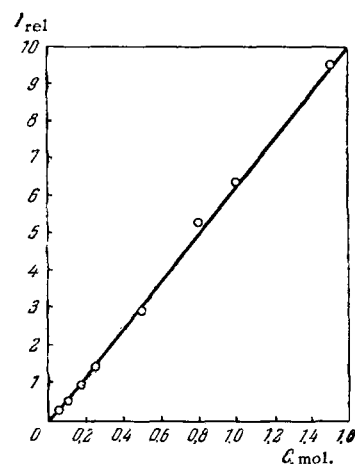


FIG. 20. The relation of the intensity of the $1325\text{--}1337 \text{ cm}^{-1}$ Raman band of powdered p-nitrophenetole relative to the 1380 cm^{-1} band of naphthalene to the mole fraction of the substance.^[152]

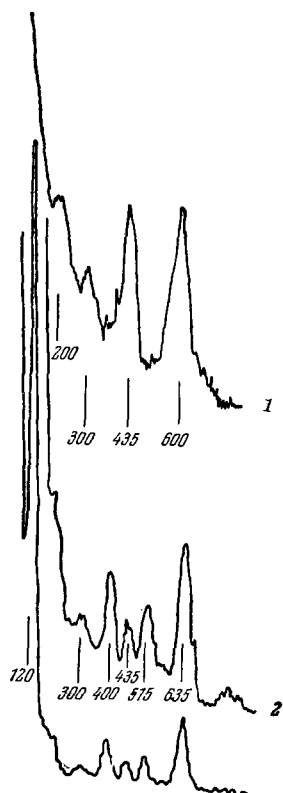


FIG. 21. Raman spectra of powdered rutile (1) and anatase (2).^[156] The latter spectrum has been recorded with two modes of amplification.

intensity of the complex band of *p*-nitrophenetole at $1325\text{--}1337\text{ cm}^{-1}$ was measured. The molar ratio of the components was varied over a wide range: from 1:20 to 1:0.66. The mean-square error, as derived from a large number of measurements (7–17), was no greater than 4.5%. We see that the proportionality between the measured intensity and the mole fraction of the substance holds over the entire concentration range. Analogous results have been obtained in studying other mixtures as well. This implies that the initial assumption on the depth of the effective layer of the substance is correct, and hence the method of measurement can be applied not only to colorless powders, but also, in any case, to weakly colored ones. This extends the range of problems and objects of study that are amenable to quantitative studies using Raman spectra.

Conclusions. In recent years the solution of the problem of obtaining Raman spectra from powdered substances has advanced considerably.

One variant of the solution consists in perfecting the method of using supplementary interference filters within the framework of photographic recording of spectra. These light filters quite effectively eliminate the continuous background in the region of the most important vibrational bands. Hence, by using this method, and taking long exposures, it has been pos-

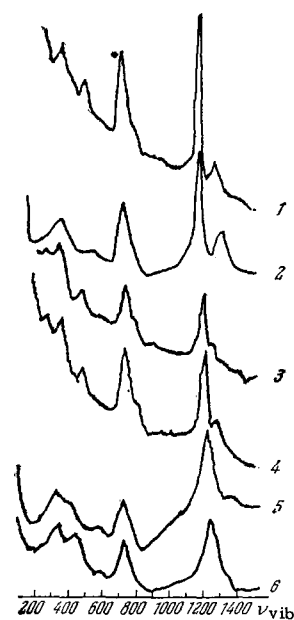


FIG. 22. Raman spectra of some metaphosphate glasses: 1 – $\text{Na}_2\text{O-P}_2\text{O}_5$; 2 – $\text{CaO-P}_2\text{O}_5$; 3 – $\text{ZnO-P}_2\text{O}_5$; 4 – $\text{MgO-P}_2\text{O}_5$; 5 – $\text{Al}_2\text{O}_3\text{-}3\text{P}_2\text{O}_5$; 6 – $\text{BeO-P}_2\text{O}_5$. The glasses were studied in the form of finely-crushed particles.^[153]

sible to obtain quite satisfactory spectra from a small number of poorly-scattering substances, the crystalline phosphates.^[150]

Another variant is based on the application of double monochromatization to the scattered radiation, and hence also of photoelectric recording of the spectra. This method still requires a large amount of the material to study. Nevertheless, it eliminates the continuous background quite radically, and makes it possible to obtain very quickly quantitative information on the entire spectrum, including even the low-frequency region (down to $20\text{--}40\text{ cm}^{-1}$). The intensive development of the photoelectric technique permits us to expect an increase in the threshold sensitivity of this method. Thus we must consider it very promising. We can get a picture of the results already obtained, e.g., from^[153-157],

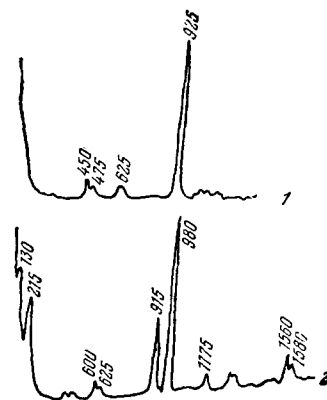


FIG. 23. Raman spectra of powdered AgClO_4 (1) and its benzene complex (2).^[157]

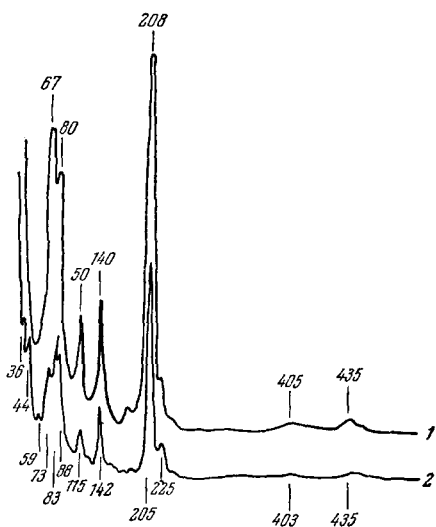


FIG. 24. Raman spectra of AlBr₃ molecules. 1 - Liquid, 2 - powder.^[156]

as well as from the spectra of various powders and inhomogeneous glasses given in Figs. 21-24.

B. Gases and Vapors at Moderate Pressures

Essentially new possibilities of studying Raman spectra in gases have arisen from the application by Stoicheff^[73] and by Welsh et al.^[72] of multiple-pass reflecting cuvettes. A detailed description of the construction of these cuvettes and their principle of action can be found in the review^[15] (see also^[3]). A subsequent important step in the perfection of the technical means of studying gases involved the use of photoelectric recording. Shortly after the first experiments of this sort,^[159] various authors have built quite reliable apparatus permitting precise quantitative measurements in the spectra of gases and vapors at relatively low pressures. Thereby they could obtain valuable information on the structures of molecules and the mechanism of their interaction.^[160,161] We shall give a brief characterization of this apparatus.

The apparatus described by Yoshino and Bernstein^[160] is built about the autocollimating spectrometer of White, Alpert, and DeBell^[92], which has a flat diffraction grating (ruled area 102×102 mm, 1200 lines/mm), and an off-axis parabolic mirror ($d = 120$ mm, $F = 750$ mm). The linear dispersion of the instrument in the working region of the spectrum amounts to 40-60 cm⁻¹/mm. Six straight Toronto-type mercury lamps with supplementary cooling of the working section (which is 900 mm long) serve to excite the spectra. The multiple-pass cuvette is quite analogous to those described in^[72] and^[73]. The lamps are located in a housing coated on the inside with a layer of magnesium oxide to increase the light yield. The apparatus was adapted to measure the degree of depolarization ρ of the lines by the method of

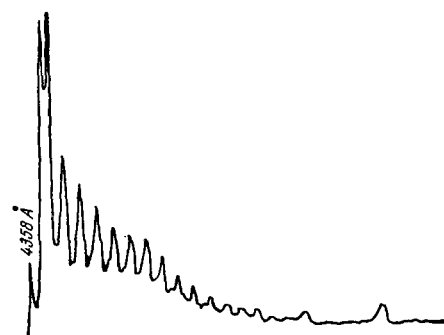


FIG. 25. Rotational Raman spectrum of gaseous N₂ molecules.^[160] Pressure = 2 atm, slit width 1.7 cm⁻¹.

Edsall and Wilson.^[20] Here a special treatment was made of the problem of the effect of the specular reflections in the multiple-pass cuvette on the measured value of ρ . With the aid of this apparatus, the spectra of many gases and vapors have been studied, in particular, the hydrocarbons.^[160,162] A combined study of the intensity and polarization of the lines permitted the authors to calculate the tensor invariants $\partial\alpha/\partial q$ of various molecules. To give a picture of the effectiveness of the apparatus, Figs. 25 and 26 give some spectra. Typical conditions of recording are: pressure = 1-2 atm slit width = 1.5-5 cm⁻¹.

The apparatus assembled by Bazhulin and Lazarev^[161] permits one to perform intensity measurements on the contours of the rotational and vibrational Raman lines of gases and vapors at pressures of 1-10 atm over the temperature range 30-250°C. The DFS-4 spectrometer^[79] is used in the apparatus; it has about twice as great a linear dispersion as that described in^[92]. The length of the multiple-pass cuvette amounts to 600 mm. The cuvette is sealed with gaskets made of the fluorinated plastics SKF-32 and SKF-26, which are chemically and thermally very stable. The spectra are excited by two linear low-pressure mercury lamps. In this apparatus, a study has been made of the pure gases H₂, O₂, N₂, CO₂, and CH₄, and also on mixtures of them with the inert gases, in connection with the problem of broadening of Raman lines.^[161] The apparatus has also made it possible to make experimen-

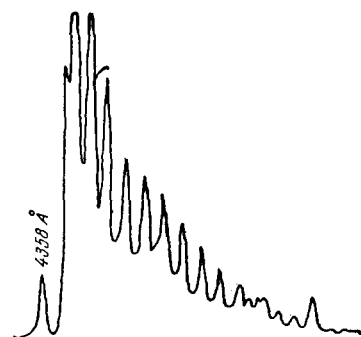


FIG. 26. Rotational Raman spectrum of gaseous O₂ molecules.^[160] Pressure = 2 atm, slit width 2.2 cm⁻¹.

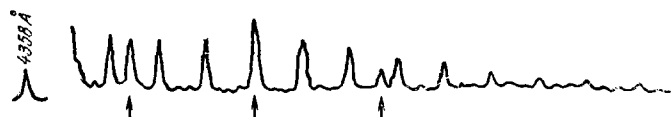


FIG. 27. Rotational Raman spectrum of gaseous O_2 molecules.^[161] Pressure = 3 atm, slit width 9.7 cm^{-1} . The arrows indicate ghosts.

tally-difficult comparative measurements of the intensities of vibrational lines of substances in the liquid and vapor states.^[39] Rotational spectra have been recorded at slit widths of $0.5\text{--}0.6\text{ cm}^{-1}$, vibrational spectra at $0.3\text{--}1.5\text{ cm}^{-1}$, and rotational-vibrational spectra at $2\text{--}3\text{ cm}^{-1}$. Figure 27 shows a sample of a recording of a rotational spectrum.

C. Gases and Vapors at High Pressures

In order to reveal the fine details in the spectrum of a gaseous substance, one often has to work at an increased pressure of the gas or vapor. There are also associated with the high-pressure technique some spectroscopic studies of great theoretical importance, namely, studies of the physical processes accompanying the condensation of a substance. A number of authors have built cuvettes suitable for solving such problems.

A good high-pressure cuvette must have a sufficient reserve of mechanical strength, and at the same time permit effective illumination of the working cavity. These requirements are contradictory, and are satisfied by compromising. The cuvette designed and built by Mikhaïlov^[163] is designed for pressures up to 250 atm. It is made from a thick-walled metal tube with three slots along generators of the cylinder for the exciting beam, and a side opening for the scattered beam. It is illuminated by three PRK-2 lamps. Cylindrical lenses made of organic glass serve to focus the light of the lamp. They are thus the windows of the cuvette. Inside the metal tube is mounted a mirror system for multiple reflection. When working with the HUET V-III spectrograph, exposures of from three to forty hours are required. With the aid of this apparatus, the effect has been studied of the pressure and temperature on the vibrational and rotational spectra of nitrogen, oxygen, and methane, and the results have been com-

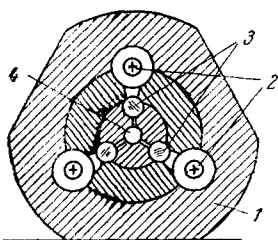


FIG. 28. Diagram of a cuvette to study Raman spectra of highly compressed gases. 1 - Shell; 2 - lamps with water filters; 3 - cylindrical lenses; 4 - scattering volume.^[163]

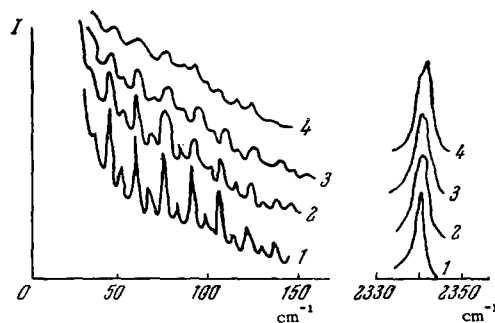


FIG. 29. Rotational and vibrational Raman spectra of N_2 molecules at various gas pressures: 1 - 15; 2 - 25; 3 - 40; and 4 - 50 atm.^[163]

pared with the collision theory of line broadening.^[164] The study carried out is of great significance. Figure 28 shows a diagram of the cuvette, and Fig. 29 shows the rotational spectrum of the N_2 molecule at various gas pressures up to 50 atm.

A cuvette designed for even higher pressures (up to 2500 atm) is described in^[165]. The cuvette was applied to study liquids, but in the opinion of the authors, it is also suitable for working with compressed gases.

The scattering cavity of the cuvette is a channel of diameter 20 mm in a metal cylinder pressed into another cylinder of outer diameter 160 mm (Fig. 30). The material introduced into the channel is illuminated through three side windows. The end window serves for exit of the scattered beam. The window seals are constructed according to the unsupported-area principle. The spectra are excited by three PRK lamps. The light on the sample is condensed with high-aperture condensing lenses. The efficiency of this cuvette is apparently not very high, as judged by the exposures (4-6 hours) required to photograph the spectra of liquid toluene and cumene using the ISP-51 spectrograph and a high-aperture camera.

The problem of efficient illumination of a highly compressed gas is very ingeniously solved in the cuvette built by Stryland and May.^[166] The idea is based on the fact that the strength of glass in compression is 10-15 greater than in tension. Correspondingly, a

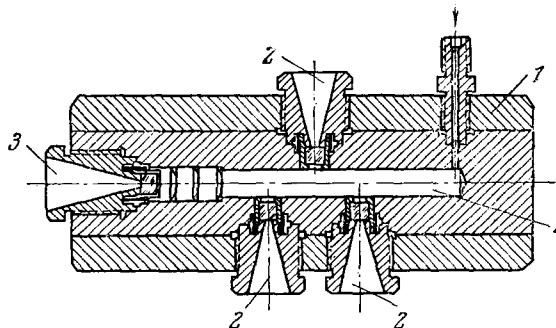


FIG. 30. Diagram of a cuvette to study Raman spectra of highly compressed liquids and gases. 1 - Shell; 2 - windows for illumination; 3 - window for observation; 4 - scattering volume.^[165]

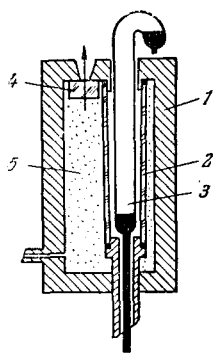


FIG. 31. Diagram of a cuvette to study Raman spectra of highly compressed gases. 1 — Shell; 2 — thick-walled glass tube; 3 — lamp; 4 — quartz window; 5 — scattering volume.^[166]

closed metal vessel containing the gas at high pressure (up to 2500 atm) is illuminated from within. To do this, a thick-walled pyrex tube is fastened eccentrically with nylon and neoprene gaskets into the vessel, which is about 460 mm long and 127 mm in diameter. A specially-designed low-pressure mercury lamp made of glass tubing of inner diameter 8 mm is inserted into it. The scattered light beam passes through an opening in the vessel, which is closed by a thick-walled quartz window seated on a ground contact. A diagram of the cuvette is shown in Fig. 31. Using this cuvette, a study has been made of the Raman spectra of hydrogen and methane over the pressure range 100—2300 atm. Shifts were noted in the vibrational lines, which cannot be explained by the change in the density of the medium.^[167]

Conclusions. The further development and perfection of methods of studying Raman spectra in gases has led to the invention of photoelectric apparatus permitting precise measurements of the intensities and polarizations of lines and bands at rather high resolution. New cuvettes have been built for working with gases at high or very high pressures.

¹M. M. Sushchinskiĭ, Tr. FIAN 5, 185 (1950).

²R. F. Stamm and C. F. Salzman Jr., J. Opt. Soc. Am. 43, 126 (1953).

³Ya. S. Bobovich and V. M. Pivovarov, UFN 60, 689 (1956).

⁴J. Brandmüller and H. Moser, Z. angew. Phys. 8, 142 (1956); 9, 567 (1957).

⁵O. D. Dmitrievskiĭ and V. A. Nikitin, Opt.-mekhan. prom., No. 4, 9 (1957).

⁶Dmitrievskiĭ, Neporent, and Nikitin, UFN 64, 447 (1958).

⁷S. G. Rautian, UFN 66, 475 (1958); Soviet Phys. Uspekhi 1, 245 (1959).

⁸J. Brandmüller, Z. analyt. Chem. 170, 29 (1959).

⁹G. G. Petrash, Optika i Spektroskopiya 6, 792 (1959); 8, 122 (1960); Optics and Spectroscopy (Opt. Soc. Am.) 6, 516 (1959); 8, 60 (1960).

¹⁰A. C. Menzies, Rev. univers. mines 15, 470 (1959).

¹¹P. A. Bazhulin and M. M. Sushchinskiĭ, UFN 68, 135 (1959); Soviet Phys. Uspekhi 2, 436 (1959).

¹²H. W. Schrötter, Z. angew. Phys. 12, 275 (1960).

¹³H. W. Schrötter, Z. Elektrochem. 64, 853 (1960).

¹⁴E. V. Chisler, Optika i Spektroskopiya 8, 359 (1960); Optics and Spectroscopy (Opt. Soc. Am.) 8, 187 (1960).

¹⁵B. P. Stoicheff, Advances Spectr., Vo. 1, 1959.

¹⁶G. Placzek, The Rayleigh and Raman Scattering, Lawrence Radiation Laboratory, Univ. of Calif., Livermore, Calif., 1959, translated from Handbuch der Radiologie 1934; Russ. Transl., Khar'kov, ONTIU, 1935.

¹⁷Vol'kenshteĭn, El'yashevich, and Stepanov, Kolebaniya molekul (Vibrations of Molecules), Vol. 2, M., Gostekhizdat, 1949.

¹⁸Kondilenko, Korotkov, and Strizhevskiĭ, Optika i Spektroskopiya 8, 471 (1960); Optics and Spectroscopy (Opt. Soc. Am.) 8, 249 (1960).

¹⁹H. J. Bernstein and G. Allen, J. Opt. Soc. Am. 45, 237 (1955).

²⁰J. T. Edsall and E. B. Wilson, Jr., J. Chem. Phys. 6, 124 (1938).

²¹D. H. Rank and R. E. Kagarise, J. Opt. Soc. Am. 40, 89 (1950).

²²Ya. S. Bobovich and D. B. Gurevich, DAN SSSR 85, 521 (1952); JETP 27, 318 (1954).

²³Long, Milner, and Thomas, Proc. Roy. Soc. A237, 197 (1956).

²⁴Yu. I. Naberukhin, Optika i Spektroskopiya 13, 498 (1962); Optics and Spectroscopy (Opt. Soc. Am.) 13, 278 (1962).

²⁵D. G. Rea, J. Opt. Soc. Am. 49, 90 (1959).

²⁶A. I. Sokolovskaya and S. G. Rautian, Optika i Spektroskopiya 6, 51 (1959); Optics and Spectroscopy 6, 29 (1959).

²⁷L. A. Woodward and J. H. B. George, Nature 167, 193 (1951); Proc. Phys. Soc. B64, 780 (1951).

²⁸G. G. Slyusarev, Geometricheskaya optika (Geometric Optics), M., Izd-vo AN SSSR, 1946.

²⁹L. G. Fedorovich and Ya. S. Bobovich, JETP 20, 1139 (1950).

³⁰G. G. Slyusarev and V. M. Chulanovskiĭ, ZhTF 18, 665 (1948).

³¹V. B. Veĭnberg and D. K. Sattarov, Opt.-mekhan. prom., No. 12, 42 (1961); No. 2, 19 (1963).

^{32a}I. L. Babich, Abstract of candidate's dissertation (Khar'kov, 1946).

^{32b}B. S. Neporent and N. G. Bakhshiev, Optika i Spektroskopiya 5, 634 (1958).

³³N. G. Bakhshiev, ibid. 7, 52 (1959); 10, 717 (1961); Optics and Spectroscopy (Opt. Soc. Am.) 7, 29 (1959); 10, 379 (1961).

³⁴O. P. Girin and N. G. Bakhshiev, UFN 79, 235 (1963); Soviet Phys. Uspekhi 6, 106 (1963).

³⁵V. M. Pivovarov, Optika i Spektroskopiya 6, 101 (1959); Optics and Spectroscopy (Opt. Soc. Am.) 6, 60 (1959).

- ³⁶ Ya. I. Frenkel', *Kineticheskaya teoriya zhidkostei* (Kinetic Theory of Liquids), M., Izd. AN SSSR, 1945; Engl. Transl., Oxford, Clarendon Press, 1946.
- ³⁷ D. G. Rea, *J. Mol. Spectr.* **4**, 507 (1960).
- ³⁸ K. H. Illinger and D. F. Freeman, *ibid.* **9**, 191 (1962).
- ³⁹ A. I. Sokolovskaya, *Optika i Spektroskopiya* **11**, 478 (1961); *Optics and Spectroscopy* (Opt. Soc. Am.) **11**, 259 (1961).
- ⁴⁰ Ya. S. Bobovich and T. P. Tulub, *JETP* **30**, 189 (1956); *Soviet Phys. JETP* **3**, 116 (1956).
- ⁴¹ V. M. Pivovarov and Ya. S. Bobovich, *Optika i Spektroskopiya* **3**, 134 (1957).
- ⁴² H. J. Bernstein, *Pure and Appl. Chem.* **4**, 23 (1962).
- ⁴³ S. A. Tare and H. W. Thompson, *Spectrochim. Acta* **18**, 1095 (1962).
- ⁴⁴ J. B. Jesson and H. W. Thompson, *Proc. Roy. Soc. A* **268**, 68 (1962).
- ⁴⁵ G. H. J. Facer and H. W. Thompson, *ibid.* **A268**, 79 (1962).
- ⁴⁶ Ya. S. Bobovich, *DAN SSSR* **98**, 39 (1954).
- ⁴⁷ A. I. Sokolovskaya and P. A. Bazhulin, *Fiz. sb. L'vovskogo gos. un-ta* **3**(8), 225 (1957).
- ⁴⁸ Ya. S. Bobovich and T. P. Tulub, *Optika i Spektroskopiya* **9**, 747 (1960); *Optics and Spectroscopy* (Opt. Soc. Am.) **9**, 396 (1960).
- ⁴⁹ T. P. Tulub and Ya. S. Bobovich, *ibid.* **9**, 669 (1960); *Optics and Spectroscopy* (Opt. Soc. Am.) **9**, 352 (1960).
- ⁵⁰ V. M. Pivovarov and Ya. S. Bobovich, *ibid.* **6**, 249 (1959); *Optics and Spectroscopy* (Opt. Soc. Am.) **6**, 160 (1959).
- ⁵¹ A. I. Sokolovskaya, *ibid.* **9**, 582 (1960); *Optics and Spectroscopy* (Opt. Soc. Am.) **9**, 307 (1960).
- ⁵² Kondilenko, Korotkov, and Strizhevskii, *ibid.* **9**, 26 (1960); *Optics and Spectroscopy* (Opt. Soc. Am.) **9**, 13 (1960).
- ⁵³ I. I. Kondilenko and V. L. Strizhevskii, *ibid.* **11**, 262 (1961); *Optics and Spectroscopy* (Opt. Soc. Am.) **11**, 137 (1961).
- ⁵⁴ M. Ya. Tsenter and Ya. S. Bobovich, *DAN SSSR* **146**, 333 (1962), *Soviet Phys. Doklady* **7**, 316 (1963).
- ⁵⁵ M. Ya. Tsenter and Ya. S. Bobovich, *Optika i Spektroskopiya* **16**, 246 (1964).
- ⁵⁶ M. Ya. Tsenter and Ya. S. Bobovich, *ibid.* (in press).
- ⁵⁷ P. P. Shorygin and A. Kh. Khalilov, *DAN SSSR* **81**, 1031 (1951).
- ⁵⁸ P. P. Shorygin and A. N. Finkel'shtein, *Zhur. Fiz. Khim.* **26**, 1272 (1952).
- ⁵⁹ P. P. Shorygin and L. Z. Osityanskaya, *DAN SSSR* **98**, 51 (1954).
- ⁶⁰ M. M. Sushchinskiĭ and V. A. Zubov, *Optika i Spektroskopiya* **13**, 766 (1962); *Optics and Spectroscopy* (Opt. Soc. Am.) **13**, 434 (1962).
- ⁶¹ R. D. Fisher and E. R. Lippincott, *Spectrochim. Acta* **6**, 255 (1954).
- ⁶² Z. Kecki, *Roczniki chemii* **30**, 921 (1956).
- ⁶³ G. Michel and G. Duyckaerts, *Spectrochim. Acta* **8**, 356 (1957).
- ⁶⁴ J. Behringer, *Z. Elektrochem.* **62**, 545 (1958).
- ⁶⁵ Lippincott, Sabilia, and Fisher, *J. Opt. Soc. Am.* **49**, 83 (1959).
- ⁶⁶ J. Behringer, *Adv. Mol. Spectr.* **3**, 1087 (1962).
- ⁶⁷ G. Michel and H. Martin, *Adv. Mol. Spectr.* **3**, 1105 (1962).
- ⁶⁸ Ya. S. Bobovich and V. V. Perekalin, *Zhur. Strukt. Khim.* **1**, 313 (1960).
- ⁶⁹ Bobovich, Kvitko, and Perekalin, *DAN SSSR* **139**, 1392 (1961).
- ⁷⁰ Bobovich, Lipina, and Perekalin, *Zhur. Strukt. Khim.* **5** (1964).
- ⁷¹ J. A. Koningstein and H. J. Bernstein, *Spectrochim. Acta* **18**, 1249 (1962).
- ⁷² Welsh, Stansbury, Romanko, and Feldman, *J. Opt. Soc. Am.* **45**, 338 (1955).
- ⁷³ B. P. Stoicheff, *Can. J. Phys.* **32**, 330 (1954).
- ⁷⁴ H. Stammreich and R. Forneris, *Spectrochim. Acta* **17**, 775 (1961).
- ⁷⁵ Stammreich, Forneris, and Tavares, *ibid.* **17**, 1173 (1961).
- ⁷⁶ N. G. Gerasimova and A. V. Yakovleva, *PTÉ*, No. 1, 83 (1956); *Opt.-mekhan. prom.* **1**, 4 (1956).
- ⁷⁷ Hilger. *Equipment of Raman Spectroscopy*, Catalog CH 334/2.
- ⁷⁸ *Spektrograf ISP-51. Opisanie i rukovodstvo k pol'zovaniyu* (The ISP-51 Spectrograph. Description and Directions for Use), *Opt.-mekhan. zavod im. OGPU, Lensovnarkhoz.*
- ⁷⁹ V. K. Prokof'ev, *Izv. AN SSSR, ser. Fiz.* **18**, 643 (1954).
- ⁸⁰ J. Brandmüller and H. Moser, *Z. angew. Phys.* **8**, 95 (1956).
- ⁸¹ B. A. Kiselev, *Optika i Spektroskopiya* **1**, 597 (1956).
- ⁸² Berkovich, Gofren, Lobachev, Fal'k, and Sharonov, *ibid.* **6**, 824 (1959); *Optics and Spectroscopy* (Opt. Soc. Am.) **6**, 539 (1959).
- ⁸³ *Studies in Spectrophotometry*, *Chem. and Eng. News* **33**, 4232 (1955).
- ⁸⁴ W. A. Wildhack, *Rev. Sci. Instr.* **27**, 113 (1956).
- ⁸⁵ D. E. Nicholson, *Anal. Chem.* **32**, 1634 (1960).
- ⁸⁶ W. A. Shurcliff, *J. Opt. Soc. Am.* **39**, 1048 (1949).
- ⁸⁷ Zubov, Petrash, and Sushchinskiĭ, *Optika i Spektroskopiya* **6**, 827 (1959); *Optics and Spectroscopy* (Opt. Soc. Am.) **6**, 541 (1959); *PTÉ* **5**, 119 (1959).
- ⁸⁸ I. M. Levin, *Diploma study* (LITMO, 1961).
- ⁸⁹ Abramson, Kononov, Mogilevskii, Murzin, and Slavnyi, *Zav. lab.* **28**, 875 (1962).
- ⁹⁰ Heigl, Black, and Wilson, *Anal. Chem.* **22**, 154 (1950).
- ⁹¹ M. L. Sosinskiĭ, *Optika i Spektroskopiya* **6**, 405 (1959); *Optics and Spectroscopy* (Opt. Soc. Am.) **6**, 254 (1959).
- ⁹² White, Alpert, and DeBell, *J. Opt. Soc. Am.* **45**, 154 (1955).
- ⁹³ E. R. Shull, *J. Opt. Soc. Am.* **45**, 670 (1955).
- ⁹⁴ L. A. Woodward and D. H. Waters, *J. Sci. Instr.* **34**, 222 (1957).

- ⁹⁵ G. Schreiber, *Exp. Techn. Phys.* **6**, 85 (1958).
- ⁹⁶ V. I. Tyulin and V. M. Tatevskii, *Optika i Spektroskopiya* **14**, 582 (1963); *Optics and Spectroscopy (Opt. Soc. Am.)* **14**, 308 (1963).
- ⁹⁷ Brochure from the firm Quarzlampen Gesellschaft (Hanau, West Germany); Exhibition of instruments in Moscow (November, 1960).
- ⁹⁸ É. V. Chisler, *PTÉ*, No. 1, 164 (1962).
- ⁹⁹ Pliva, Schneider, Stokr, and Ulbert, *Spectrochim. Acta* **11**, 499 (1957) (Proceedings of the Colloquium Spectroscopicum Internationale VI, Amsterdam, May, 1956); *Rev. un. mines* **15**, 483 (1959).
- ¹⁰⁰ I. I. Kondilenko and G. A. Vorob'eva, *Optika i Spektroskopiya* **9**, 524 (1960); *Optics and Spectroscopy (Opt. Soc. Am.)* **9**, 273 (1960); *PTÉ* **2**, 142 (1961).
- ¹⁰¹ H. Moser and D. Stieler, *Z. angew. Phys.* **12**, 280 (1960).
- ¹⁰² G. Geppert and R. Scholz, *Monatsb. d. Deutsch. Akad. Wiss. (Berlin)* **4**, 8 (1962).
- ¹⁰³ M. Bridoux and M. Delhaye, *J. phys. et le radium* **23**, 334 (1962).
- ¹⁰⁴ K. W. F. Kohlrausch, *Ramanspektren*, Akad. Verlagsgesell. Becker + Erler, 1943; *Russ. Transl., M., IL*, 1952.
- ¹⁰⁵ H. Stammreich, *Spectrochim. Acta* **8**, 41 (1956).
- ¹⁰⁶ M. M. Delhaye, *Spectrochim. Acta* **11**, 485 (1957) (cf. Ref. 99, part 1).
- ¹⁰⁷ H. Stammreich, *Pure and Appl. Chem.* **4**, 97 (1962).
- ^{108a} Kir'yanova, Pivovarov, and Yakovlev, *Optika i Spektroskopiya* **13**, 79 (1962); *Optics and Spectroscopy (Opt. Soc. Am.)* **13**, 43 (1962).
- ^{108b} Pivovarov, Kir'yanova, Bobovich, and Tarkhov, *ibid.* **7**, 258 (1959); *Optics and Spectroscopy* **7**, 163 (1959).
- ¹⁰⁹ F. T. King and E. R. Lippincott, *J. Opt. Soc. Am.* **46**, 661 (1956).
- ¹¹⁰ Miller, Carlson, and White, *Spectrochim. Acta* **15**, 709 (1959).
- ¹¹¹ Ablekov, Zaitsev, and Pesin, *PTÉ* **2**, 140 (1961).
- ¹¹² Ablekov, Pesin, and Fabelinskiĭ, *JETP* **39**, 892 (1960); *Soviet Phys. JETP* **12**, 618 (1961).
- ¹¹³ N. S. Ham and A. Walsh, *Spectrochim. Acta* **12**, 88 (1958); *J. Chem. Phys.* **36**, 1096 (1962).
- ¹¹⁴ Powell, Lippincott, and Steele, *Spectrochim. Acta* **17**, 880 (1961).
- ¹¹⁵ F. A. Miller and G. L. Carlson, *Spectrochim. Acta* **16**, 6 (1960).
- ¹¹⁶ M. M. Delhaye, *J. phys. et le radium* **20**, 47 (1959).
- ¹¹⁷ M. M. Delhaye and M. B. Delhaye-Buisset, *Rev. un. mines* **15**, 480 (1959).
- ¹¹⁸ M. M. Delhaye, *Publ. Graupem. avancem. methodes spectrogr.* (May-June, 1961), p. 243; *Adv. Mol. Spectr.* **3**, 1286 (1962).
- ¹¹⁹ F. Valentin, *Compt. Rend.* **244**, 1915 (1957).
- ¹²⁰ Valentin, Dumartin, and Biron, *J. phys. et le radium* **18**, 64S (1957).
- ¹²¹ S. P. S. Porto and D. L. Wood, *J. Opt. Soc. Am.* **52**, 251 (1962).
- ¹²² Eckhardt, Hellwarth, McClung, Schwarz, and Weiner, *Phys. Rev. Letters* **9**, 455 (1962).
- ¹²³ *Electronics* **36**, 74 (1963); *Electronic News* **8**, No. 373, 12 (1963); *Electronic Design* **11**(1), 12 (1963); *Sci. News Letts.* **82**(24), 378 (1963); *Electr. Eng.* **82**(1), 41 (1963).
- ¹²⁴ F. J. McClung and D. Weiner, *J. Opt. Soc. Am., Suppl. No. 2*, 21 (1963).
- ¹²⁵ Geller, Bortfeld, Soog, and Woodsbury, *Proc. IEEE* **51**(9), 1236 (1963).
- ¹²⁶ R. W. Hellwarth, *Phys. Rev.* **130**, 1850 (1963); *Appl. Opt.* **2**, 847 (1963).
- ¹²⁷ G. Riveire and R. Dupeyrat, *Compt. rend.* **256**, 1947 (1963).
- ¹²⁸ Chien, J.-Y. and P. Bender, *J. Chem. Phys.* **15**, 376 (1947).
- ¹²⁹ J. Brandmüller and H. Schrötter, *Z. Phys.* **149**, 131 (1957).
- ¹³⁰ R. Donaldson, *J. Sci. Instr.* **29**, 150 (1952).
- ¹³¹ D. H. Rank and J. S. McCartney, *J. Opt. Soc. Am.* **38**, 279 (1948).
- ¹³² H. Moser, *Spectrochim. Acta* **11**, 490 (1957) (cf. Ref. 99, part 1).
- ¹³³ A. W. Reitz, *Z. Phys. Chem.* **B46**, 181 (1940).
- ¹³⁴ W. Guber and K. H. Riggert, *Z. Naturforsch.* **6a**, 464 (1951).
- ¹³⁵ Simon, Kriegsman, and Steger, *Z. phys. Chem.* **205**, 181 (1956).
- ¹³⁶ J. Brandmüller and E. Schmid, *Z. Phys.* **144**, 428 (1956).
- ¹³⁷ G. Heinz and A. Simon, *Z. phys. Chem.* **216**, 67 (1961).
- ¹³⁸ M. C. Tobin, *J. Opt. Soc. Am.* **49**, 850 (1959).
- ¹³⁹ Ya. S. Bobovich and V. M. Pivovarov, *DAN SSSR* **97**, 801 (1954).
- ¹⁴⁰ Danil'tseva, Zubov, Sushchinskiĭ, and Shuvalov, *JETP* **44**, 2193 (1963); *Soviet Phys. JETP* **17**, 1473 (1963).
- ¹⁴¹ Ya. S. Bobovich and V. M. Pivovarov, *JETP* **29**, 693 (1955), *Soviet Phys. JETP* **2**, 357 (1956).
- ¹⁴² Ferraro, Ziomeck, and Mack, *Spectrochim. Acta* **17**, 802 (1961).
- ¹⁴³ J. Behringer and J. Brandmüller, *Z. angew. Phys.* **14**, 674 (1962).
- ¹⁴⁴ K. W. F. Kohlrausch, *Der Smekal-Raman-Effekt*, J. Springer, Berlin (1931).
- ¹⁴⁵ J. Cabannes, *Compt. rend.* **223**, 301 (1946).
- ¹⁴⁶ J. Brandmüller and H. Moser, *Einführung in die Ramanspektroskopie*, D. Steinkopff Verlag, Darmstadt, 1962.
- ¹⁴⁷ G. Bergmann and G. Thimm, *Naturwiss.*, No. 15, 359 (1958).
- ¹⁴⁸ G. Bergmann, *Rev. univers. mines* **15**, 484 (1959).
- ¹⁴⁹ Schreder, Nerdel, and Kreuzze, *Z. analyt. Chem.* **170**, 43 (1959).
- ¹⁵⁰ E. Steger and A. Simon, *Z. anorg. allg. Chem.* **294**, 1 (1958).
- ¹⁵¹ F. Vratny and R. B. Fisher, *Appl. Spectr.* **14**, 76 (1960).

- ¹⁵² Ya. S. Bobovich and Ya. A. Ėĩdus, *Optika i Spektroskopiya* **16**, 424 (1964).
- ¹⁵³ Ya. S. Bobovich, *ibid.* **16**, 417 (1964); **13**, 459, 492 (1962); **14**, 647 (1963); *Optics and Spectroscopy (Opt. Soc. Am.)* **16**, 228 (1964); **13**, 254, 274 (1962); **14**, 342 (1963).
- ¹⁵⁴ Ya. S. Bobovich and T. P. Tulub, *Optika i Spektroskopiya* **12**, 489 (1962); *Optics and Spectroscopy (Opt. Soc. Am.)* **12**, 269 (1962).
- ¹⁵⁵ Ya. S. Bobovich and G. T. Petrovskii, *Zhur. Strukt. Khim.* **4**, 765 (1963).
- ¹⁵⁶ Ya. S. Bobovich and D. K. Arkhipenko, *Optika i Spektroskopiya* **17**, No. 5 (1964).
- ¹⁵⁷ Sh. Sh. Raskin, *DAN SSSR* **141**, 900 (1961).
- ¹⁵⁸ E. V. Pershina and Sh. Sh. Raskin, *Optika i Spektroskopiya* **13**, 488 (1962); *Optics and Spectroscopy (Opt. Soc. Am.)* **13**, 272 (1962).
- ¹⁵⁹ V. M. Pivovarov and Ya. S. Bobovich, *ZhTF* **26**, 649 (1956); *Soviet Phys.-Tech. Phys.* **1**, 624 (1957).
- ¹⁶⁰ T. Yoshino and H. J. Bernstein, *Spectrochim. Acta* **10**, 227 (1957); *J. Mol. Spectr.* **2**, 213 (1958).
- ¹⁶¹ P. A. Bazhulin and Yu. A. Lazarev, *Optika i Spektroskopiya* **8**, 206 (1960); *Optics and Spectroscopy (Opt. Soc. Am.)* **8**, 106 (1960).
- ¹⁶² T. Yoshino and H. J. Bernstein, *J. Mol. Spectr.* **2**, 241 (1958); *Spectrochim. Acta* **14**, 127 (1959).
- ¹⁶³ G. V. Mikhaĩlov, *JETP* **36**, 1368 (1959), *Soviet Phys. JETP* **9**, 974 (1959).
- ¹⁶⁴ G. V. Mikhaĩlov, *JETP* **37**, 1570 (1959), *Soviet Phys. JETP* **10**, 1114 (1960); *Optika i Spektroskopiya* **12**, 646 (1962); *Optics and Spectroscopy (Opt. Soc. Am.)* **12**, 361 (1962).
- ¹⁶⁵ Gonikberg, Sterin, Ukholin, Opekunov, and Aleksanyan, *Optika i Spektroskopiya* **6**, 109 (1959); *Optics and Spectroscopy (Opt. Soc. Am.)* **6**, 66 (1959).
- ¹⁶⁶ J. C. Stryland and A. D. May, *Rev. Sci. Instr.* **31**, 414 (1959).
- ¹⁶⁷ May, Stryland, and Welsh, *J. Chem. Phys.* **30**, 1099 (1959).

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