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MEASUREMENT OF THE ABSOLUTE CROSS SECTIONS OF RAMAN SCATTERING OF LIGHT IN CRYSTALS, POWDERS, AND LIQUIDS

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A method is described for measuring the absolute cross sections of Raman scattering (RS) of light in single crystals, powders, and liquids. The absolute values of the RS lines of stilbene, $NaClO_3$, and benzene are determined for different temperatures. The RS cross sections for crystalline and liquid stilbene and benzene are compared, and a sharp increase of the cross sections on going from the liquid to the crystal is observed.

INTRODUCTION

AN investigation of the Raman scattering (RS) spectra in disperse media (polycrystals, powders, suspensions) is of great interest, since many natural and artificial products are bodies of just this kind. However, owing to the large difficulties of obtaining spectra of such objects, they were so far investigated very little. It should be noted that although the development of methods of obtaining and investigating RS spectra of disperse media has been going on for a long time[1-7], an extensive use of these methods for the investigation of various objects (including those having also absorption) was started only in recent years[8-11]. Progress in this field is connected to a considerable degree with the use of lasers as exciting light sources[12-17].

The problem of measuring the absolute RS cross sections of crystals is of interest in itself. Although methods of measuring absolute RS cross sections for liquids have already been developed[18-21], no such measurements were made for crystals. There are no published data on measurements of the absolute RS cross sections of disperse media.

The existing methods of obtaining RS spectra of disperse media can be divided into two classes: reflection methods and transmission methods. In reflection methods, the scattered radiation is gathered from the same surface on which the exciting radiation is incident, and in transmission methods these surfaces are separated by a layer of matter. To measure the absolute RS cross sections, transmission methods have the advantage that they make it possible to connect more simply the observed quantities with the parameters of the medium. We shall henceforth confine ourselves to transmission methods only.

The most difficult problem in the investigation of RS spectra of the sperse media is the measurement of the line intensities, which depend in a complicated manner not only on the properties of the matter but also on the characteristics of the medium (dimensions and grain form, packing coefficient, etc.). Similar problems arise in the study of the luminescence of disperse media. Ivanov was the first to attempt to take into account the influence of the disperse nature of the medium on the luminescence intensity. On the basis of Gershun's calculations[22], he obtained the dependence of the luminescence intensity on the thickness of a layer of powder[23]. It was assumed in these calculations, however, that the absorption of the luminescence light is much smaller than the absorption of the exciting light. In the investigation of RS this assumption is incorrect.

A solution of the problem in accordance with the scheme developed by Ivanov, but under more general assumptions, is given in[24]. In that paper, the scattering medium is described by two parameters: the scattering constant s, characterizing the flux reflected by infinitesimally thin flat layer of medium, and the absorption constant k. These parameters of a diffuse medium were first introduced by Schuster[25]. If it is assumed that the structure of the given object does not change with thickness, and that the light inside the scattering layer remains completely diffuse, then s and k are characteristics of the material only, and do not depend on the thickness of the layer. Then, according to[24], the dependence of the RS line intensity on the thickness of the scattering layer, in the case of transmission measurements, is given by the formula

$$I=\frac{(1+R)(1+R')\chi}{(\delta^2-R^2)(\delta'^2-R'^2)}\left[\frac{(\delta-\delta')(\delta\delta'+RR')}{L-L'}\;\frac{(R'\delta+R\delta')(\delta\delta'-1)}{L+L'}\right], \tag{1}$$

where

$$\delta=e^{Lx},\qquad L=\sqrt{2ks+k^2},\qquad R=1+k/s-\sqrt{k^2/s^2+2k/s},$$

χ is the scattering coefficient for the given RS line, R is the coefficient of reflection from an infinitely thick layer of the given substance, L is the effective attenuation coefficient, and x is the thickness of the cell. All the unprimed quantities pertain to the line of the exciting radiation, and the primed ones to the line of the scattered radiation.

In the particular case when k = k′ and s = s′, which is realized at low frequencies of the RS lines, formula (1), following certain supplementary transformations, takes the form

$$\frac{I}{x}=\frac{1}{(e^{2Lx}-R^2)^2}(1+R)^2e^{Lx}\chi\left[e^{2Lx}+R^2-\frac{R(e^{2Lx}-1)}{Lx}\right] \tag{2}$$
$$=f(R,Lx)\chi.$$

In (2) are contained two variable quantities, R and Lx. The quantity Lx can be determined by measuring the dependence of the intensity I_{ext} of the exciting light passing through the layer on the thickness of the layer.

This dependence[24] is described by the formula

$$I_{\text{exc}} = I_{\text{exc}}(0)\,e^{-Lx} \tag{3}$$

($I_{\text{ext}}(0)$ is the intensity of the exciting light at the entrance to the cell). From this it is easy to obtain the value of Lx for given objects, and only the parameter R remains unknown in (2). By measuring the intensity of the RS lines at different cell thicknesses, we obtain experimentally the quantity I/x of the left side of formula (2). The quantity R in the right side is chosen such as to satisfy relation (2). To determine this quantity it is sufficient, in principle, to have data for two values of x. Data for other values of x make it possible to evaluate the degree of agreement of formula (2) with experiment. If this agreement does not take place, then we can determine from (2) the scattering coefficient

$$\chi = I_{\text{exc}}(0)\chi_0 N, \tag{4}$$

where N is the number of scattering molecules and χ_0 the absolute RS cross section per molecule.

Measurements made in accordance with the indicated scheme have shown[26] that satisfactory agreement of the theoretical formula (2) with the results of experiment is obtained only when certain conditions are satisfied.

MEASUREMENT PROCEDURE

The investigated substance was a stilbene powder with different degrees of dispersion: the grain dimension of the first fraction was 0.1—0.2 mm, that of the second 0.2—0.3 mm, the third 0.3—0.4 mm, and the fourth 0.4—0.5 mm. Each fraction of the substance was placed in plane-parallel cells of dimension 12 mm and thickness 1, 2, 3, 4 and 5 mm. The source of exciting radiation was a PRK-2 mercury lamp (line 4358 Å), and the cell was illuminated with a parallel light beam. The integral intensity of the RS line of stilbene $\Delta\nu = 1593\ \text{cm}^{-1}$ was measured. The work was performed with the ISP-51 spectrograph by a photographic method with the photoelectric spectrometer DFS-12. The experimental setup is shown in Fig. 1a. By varying the experimental conditions we established that agreement between the experimental and theoretical plots of I/x against Lx is attained at small apertures of the radiation emerging from the scattering powder towards the spectrometer slit. In addition, the ratio of the illuminated surface of the cell to its total surface should be 0.4—0.6.

The described "transmission" procedure was used not only to investigate powders, but also almost-transparent media—liquids and single crystals. We note that in the previously cited papers, reporting measurement of the absolute RS cross section in liquids, the angle between the directions of the exciting and scattered light ranged from 90 to 20°. Under these conditions, the greatest methodological difficulty lies in the allowance for the difference in the apertures of the exciting light and the scattered light, calling for special measurements and recalculations. On the other hand, if the observation is in the same direction as the direction of the exciting light, then allowance for the aperture of the illumination is very simple. The experimental setup for the measurement of the absolute RS cross sections of liquids and single crystals is shown in Fig. 1b.

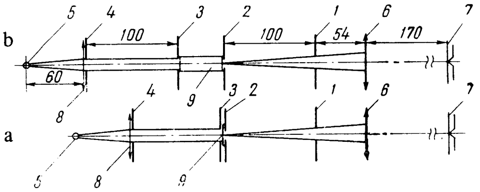

FIG. 1. Setup for the determination of the absolute cross sections of Raman scattering of light: a—in powders, b—in single crystals and liquids; 1, 2, 3, 4—diaphragms, 5—lamp, 6—condenser, 7—spectrometer slit, 8—lens, 9—cell.

MEASUREMENT RESULTS

Adhering to the foregoing conditions, we measured the integral intensities I of the RS lines of a stilbene in powder for a number of fractions and cell thicknesses, and also the integral intensity of the exciting line $I_{\text{exc}}(0)$, which was attenuated by a fixed factor during the course of registration by means of neutral filters. Knowing the number of molecules of the scattering medium in the working volume of the cell, it was possible to determine the absolute RS cross section for the given substance inside a definite solid angle per molecules, using the formula

$$\chi_0 = \frac{I}{I_{\text{exc}}(0)\,x f(R, Lx) N}. \tag{5}$$

For comparison, we determined the RS cross sections in single-crystal stilbene. The measurements were made with crystals of cylindrical form, of 15 mm diameter and 5—50 mm length. Experiment has shown that the exciting line becomes attenuated in the single crystal in accordance with (3). Experiments performed with single crystals 20 and 50 mm long gave values R = 0.008, i.e., values having little influence on the function f(R, Lx) (see (2)), as expected for R in a single crystal. It was therefore possible to assume in the subsequent calculations R = 0. Equation (5) then goes over into the following equation for the single crystal:

$$\chi_0 = \frac{I}{I_{\text{exc}}(0)\,e^{-Lx} x N}. \tag{6}$$

It is easy to see that formula (6) at L = 0 gives the absolute RS cross section of transparent liquids.

The cross sections in the powder and in stilbene single crystals were measured at different solid angles of the scattered radiation. The experiments have shown that they coincide in the single crystal and in the powder at small apertures of the emerging radiation (6° and less). The solid angle in which the RS takes place in a transparent medium can be easily obtained by integrating over the volume of the single crystal or the liquid. It is assumed that the molecules situated at a small distance r from the single-crystal axis scatter in the same solid angle as molecules situated on the axis. Simple calculation yields

$$\Delta\omega_{\text{av}} = S/ab, \tag{7}$$

where S is the working area of the condenser and a and b are the distances from the front and rear planes of the crystal to the condenser, respectively. A more accurate calculation yields practically the same expression.

Table I. Absolute RS cross sections of stilbene (1593 cm^{-1} line)

	Grain dimension and diameters of single crystal, mm	$\Delta\omega_{av}\cdot10^2$, si	$\chi_0\cdot10^{28}$, cm^{-2}
Powder	0.1÷0.2	3.34	469
	0.4÷0.5	3.33	464
Single crystal	15	2.5	460
	11	2.5	458

The results of the measurements of the absolute RS cross sections of stilbene are listed in Table I. These results were obtained under the assumption that the indicatrix of the stilbene 1593 cm^{-1} line is spherical, and recalculation with allowance for another indicatrix form entails no difficulty. The relative measurement error is ±20%. Agreement between results obtained under different conditions leads to the conclusion that this method can be used to measure the absolute cross sections of RS in powders and in single crystals.

The described procedure was used also to measure the RS cross sections in benzene powder. The measurements were made on powdered frozen benzene with grain dimensions 0.3–0.04 mm, placed in round quartz cells of 12 mm diameter and thickness 1, 2, 3, 4, and 5 mm. We measured the cross section of the 992 cm^{-1} benzene line following excitation with a mercury end-surface low-pressure lamp (4358 Å line) with an interference filter at 101, 172, and 252°K. The cells with the powder were placed in a metallic mount and were inserted together with the mount in a quartz Dewar with a ground vacuum stopper (Fig. 2). Cold nitrogen vapor was passed through the Dewar, making it possible to maintain the required temperature within 3°. The temperature was monitored with two thermocouples. The 992 cm^{-1} RS line and the 4358 Å exciting line were registered at slit widths 11 cm^{-1}, the measured quantities being the intensities at the line peaks, which under these conditions were proportional to the integral intensities.

At the same temperatures, were measured relative intensities of the RS lines of solid benzene at low frequencies relative to the 992 cm^{-1} line. The low-frequency lines of benzene and the 992 cm^{-1} line were registered at a slit width 3 cm^{-1}. The integral intensities were measured over the line contours. All this has made it possible to determine the cross sections of the Raman scattering lines of benzene at low frequencies, and their variation with the temperature. Table II and Fig. 3 show the results of these measurements.

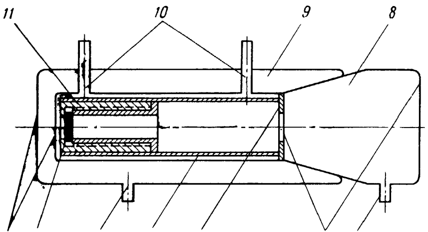

FIG. 2. Dewar for temperature measurements of the absolute cross sections of Raman scattering of light in powders: 1, 6–quartz windows, 2–cell with substance, 3 and 7–tubes for pumping out the air, 4–metallic cylinder, 5–diaphragm to limit the aperture of the emerging radiation, 8–vacuum test tube, 9–vacuum jacket, 10–tubes for the inflow and outflow of nitrogen and for the thermocouples, 11–brass insert.

Table II. Absolute RS cross sections in benzene powder (992 cm^{-1} line)

Temperature, °K	L per mm	R	$\chi_0\cdot10^{28}$, cm^2
101	0.41	0.6	46
172	0.41	0.7	55
252	0.42	0.7	55

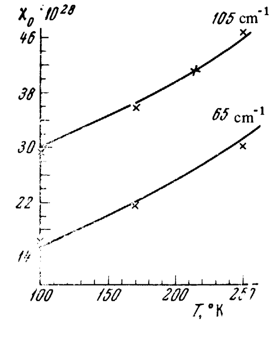

FIG. 3. Temperature dependence of absolute RS cross sections for low-frequency lines of benzene. Solid lines–theoretical plot, points–experimental data.

We measured similarly the RS cross section of the 936 cm^{-1} of NaClO$_3$ in powder. The powder, with grain dimensions 0.3–0.4 mm, was placed in cells similar to those used for the benzene. The absolute cross section of the 936 cm^{-1} line was determined at temperatures 101, 293, and 483°K. We also measured the relative intensities of the low-frequency RS lines $\Delta\nu_1$ = 123 cm^{-1}, $\Delta\nu_2$ = 131 cm^{-1} and $\Delta\nu_3$ = 179 cm^{-1}, corresponding to orientation oscillations. To this end, the crystal was chosen in the form of a cube measuring 10 × 10 × 10 mm, and the measurements were performed by means of a procedure described in[27]. The measurement results are given in Table III and in Fig. 4.

As can be seen from Tables II and III and from Figs. 3 and 4, the temperature dependence of the investigated Raman lines agrees well with the theoretical dependence. Similar conclusions were drawn earlier in[28,29].

Table III. Absolute cross section of RS of light in NaClO$_3$ powder (936 cm^{-1} line)

Temperature, °K	L per mm	R	$\chi_0\cdot10^{28}$, cm^2
101	0.67	0.2	7.7
293	0.70	0.3	7.2
483	0.53	0.3	7.9

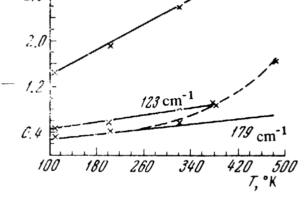

FIG. 4. Temperature dependence of the absolute RS cross sections for low-frequency NaClO$_3$ lines. Solid lines–theoretical dependence, points–experimental data.

Table IV

Substance	Aggregate state*	Cell dimensions mm	$\Delta\omega_{av}\cdot 10^3$, sr	$\chi\cdot 10^{28}$ (per unit solid angle)	$\chi_0\cdot 10^{28}$, cm^2
Stilbene $\Delta\nu = 1593$ cm^{-1}	S		25	36.8	460
	L	$d = 12$, $l = 104$	47	2.16	27
		$d = 12$, $l = 23$	20	2,0	25
Benzene $\Delta\nu = 992$ cm^{-1}	S		7.9	3.6	55
	L	$d = 26$, $l = 1050$	14	0.135	2.1
		$d = 18$, $l = 1050$	4.2	0.129	2.0

The anomalous temperature dependence of the $\Delta\nu_3 = 139$ cm^{-1} line of $NaClO_3$, connected with the phase transition in this crystal, was discussed in detail in[30].

To compare the cross sections of RS of light in solids and liquids, we measured the RS cross sections in liquid benzene at room temperature ($\Delta\nu = 992$ cm^{-1}) and stilbene at +150°C, excited by the mercury 4358 Å line. To measure the RS cross section of benzene, we used a glass Dewar 1050 mm long and 28 mm in diameter, which was illuminated with a parallel beam. The aperture of the emerging beam did not exceed 5°. The measurements were performed at different cell working diameters, which were set by means of diaphragms. The RS cross section of liquid stilbene was measured in metallic tubes of 12 mm diameter with quartz windows.

The measurement results are listed in Table IV. The measurement results of[18-20], with allowance for the scattering characteristic of the liquid benzene, yield for the 992 cm^{-1} line $\chi_0 \cdot 10^2 = 1.9$ cm^2. The data for stilbene were obtained under the assumption that the indicatrix of the 1593 cm^{-1} RS line is spherical. We call attention to the large difference between the RS cross sections in liquid and in crystal. A discussion of this phenomenon is presented in[31].

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