Hyper-Raman scattering and the selection rules for the wave vector and matrix elements in the vibrational spectra of glasses and liquids

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Results of the study of polarized hyper-Raman spectra at various scattering angles (0, 90, and 180°) in SiO_2 and TiO_2-SiO_2 glasses and in liquid CCl_4 are presented. It is concluded that in these media both polaritons and purely mechanical vibrational excitations can be characterized by a wave vector. Longitudinal-transverse splitting of dipole vibrations in the liquid is found for the first time. Exclusion of dipole modes (mutual exclusion rule) in the Raman scattering spectra of glasses and liquids is deduced by comparing the Raman scattering and hyper-Raman scattering spectra. A new approach, based on the macroscopic averaged symmetry of the media ($\infty\infty m$ symmetry), to the analysis of the selection rules in the vibrational spectra of glasses and liquid is proposed. Within the framework of this approach, an explanation is given of the experimental results on the polarization and frequency-angular dependences of the longitudinal and transverse mode intensities in the hyper-Raman scattering spectra. The appearance of mutual exclusion in the Raman scattering spectra of glasses and liquid is also explained.

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1. INTRODUCTION

At present there is no corroborated approach to the interpretation of the vibrational spectra of glasses. To explain these spectra, various representations were invoked, based on definite structural models of glass: the molecular model,[1] the crystallite models,[2–4] and the model of the spatially damped modes.[5] Common to all the approaches is the concluded proportionality of the intensity of the vibrational spectrum of glasses [of the Raman scattering (RS), IR absorption, and in elastic scattering of neutrons] to the density of the vibrational states.[6] The models of Refs. 1–5 presuppose total violation of the selection rules both with respect of the wave vector and with respect to the matrix element for the vibrational excitations of glass.

As for a liquid, its vibrational spectra are explained using the customarily assumed molecular model, in which it is presupposed that the selections rules with respect to the matrix element are the same in the spectra of liquids as for the isolated molecule.[7] The molecular model of a liquid, just as of a glass, presupposes a strong localization of the vibrations, and consequently a large indeterminacy of the wave vector of the excited vibrations in the scattering and absorption of light.

We have previously reported observation of vibrational polaritons in hyper-Raman scattering (HRS) spectra of glasses[8,9] and liquid.[10] The very fact that the polariton frequency depends on the scattering angle contradicts the assumption that the momentum conservation law is violated in the scattering process. In addition, the experimental data of the present study [longitudinal-transverse (*LO–TO*) splitting of the dipole vibrations, polarization of the *LO* and *TO* components in the spectra, the angular dependence of the *LO* and *TO* components at scattering angles from 0 to 180°] show that the wave vector can describe not only polaritons (mixed states of electromagnetic and mechanical vibrations), but also purely mechanical vibrations in glasses and in a liquid (Sec. 4.1).

Let us discuss, as least qualitatively, the extend to which the evidence of the possibility of describing vibrational excitations in glasses and liquids by a definite wave vector, i.e., the delocalization of the vibrations, is expected. It is known[11] that the vibrations in disordered media are delocalized if the characteristic height ΔU of the random potential relief, in whose fields the vibrational excitation propagates, is lower than the energy of this excitation. In the spectra of oxide glasses and liquid, the observed maxima pertain as a rule to internal vibrations (frequency $\gtrsim 200$ cm^{-1}) of the structural polyhedra—aggregates of atoms that make up the short-range order (molecules in liquid and unit cells in glass).[12] In these media the disorder has a topological character.[13] One can therefore expect in this case ΔU to be of the order of energy of the external vibration of the structural polyhedra (frequencies $\lesssim 200$ cm^{-1}), and consequently, the delocalization condition of the vibrational excitations pertaining to the internal vibrations of the polyhedra can be satisfied. It is probable that if the disorder is large and ΔU turns out to be of the order of the internal-vibration energy, the premises presented in the literature[1–6] that the vibrations are localized may turn out to be correct.

Satisfaction of the momentum conservation law in the course of scattering by vibrational states of glasses (liquids) requires that the macroscopic symmetry of the medium be taken into account in the analysis of the selection rules with respect to the matrix element, in analogy with what is done in crystals. Glasses (in the absence of internal stresses) as well as liquids (at rest, optically inactive and not liquid crystals) are isotropic media and have a macroscopic (mean-statistical) symmetry $\infty\infty m$. It is probable that an interpretation of the vibrational spectra of a condensed medium (substance) on the basis of the average symmetry is possible if the medium consists of statistically disordered elements (structural

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units), whose dimensions a are considerably smaller than the wavelength λ of the vibrations. In glasses and liquids we have $a \ll \lambda$ and consequently one can assume that each structure element of these media is in an isotropic field $\infty\infty m$.

General group-theoretical considerations for the limiting group $\infty\infty m$ (Sec. 2.1) show that the vibrational spectrum of glasses (liquids) must satisfy a mutual exclusion, according to which the dipole vibrations are forbidden in the RS spectra. In addition, allowance for the macroscopic symmetry should lead to specific polarization and angular dependences of the intensities of the *TO* and *LO* vibrations in the HRS spectra of the glasses and the liquid (Sec. 2.2).

We consider below first those distinguishing features that are expected when account is taken of the macroscopic symmetry (Sec. 2) and then report the experimental results that confirm the satisfaction of the momentum conservation law in the course of scattering by vibrational states of glasses and liquids (Sec. 4.1), as well as of the selection rules with respect to the matrix element (Sec. 4.2). An investigation of the frequency-angular and polarization dependences of the HRS spectra called for improving the system of excitation of the spectra and for the use of new optical systems, which are described in Sec. 3.

The peculiarities we observed in the vibrational spectra of oxide glasses and liquid (the validity of the momentum-conservation law, the microscopic approach to the analysis of the spectrum, and the mutual exclusion) were not predicted by anyone before. Allowance for them can not only refine our ideas concerning and vibrational states of the disordered media, but also extend the possibility of obtaining new information from vibrational spectra (for example, the degree of disorder of the medium). They should be taken into account in the future when developing a general dynamic theory of glasses (liquids). We note that when account is taken of the peculiarities observed by us, the treatment of the dynamics of the glasses and liquids can in purely formal manner differ little from the already known approaches to disordered crystals.[14–16] However, the possibility of identical approaches to the analysis of the vibrational spectra of glasses (liquids). The common character of the approaches could only mean similarity of certain properties of vibrational excitation in these condensed media.

2. MACROSCOPIC SYMMETRY AND SELECTION RULES IN THE RS AND HRS SPECTRA OF GLASSES AND LIQUIDS

The intensity of the HRS process is determined by the linear polarization $\mathbf{P}(\omega_s)$ induced by the electric field of the incident light wave $\mathbf{E}(\omega_i)$:

$$P_j(\omega_s)=\chi_{jmnl}E_m(\omega_i)E_n(\omega_i)Q_l^*(\omega_v),$$

where χ_{jmnl} is the nonlinear susceptibility of the HRS process, $Q_l^*(\omega_v)$ is the normal coordinate of the vibration of frequency ω_v, the indices j, m, n, and l denote the axes x, y, z, while ω_i and ω_s denote the frequencies of the exciting and scattered light, respectively ($\omega_s = 2\omega_i - \omega_v$). For dipole vibrations, the index l indicates in fact the polarization vibration. In our case $m = n$ and the tensor χ_{jmnl} is symmetric in the indices m and n, i.e., in the case of an isotropic medium there are only two independent components.[17] If the frequencies ω_i and ω_s are in the transparency region of the medium, the tensor χ_{jmnl} of an isotropic medium becomes symmetrical with respect to the first three indices and has only one independent component (Table I).

TABLE I. HRS tensor for an isotropic medium.

j	m, n, l									
	xxx	yyy	zzz	yyx	zzy	xxz	zzx	xxy	yyz	xyz
x	$3a$			a			a			
y		$3a$			a			a		
z			$3a$			a			a	

2.1. Mutual exclusion

It is known that an isotropic medium that has no optical activity belongs to the group of total spherical symmetry K_h ($\infty\infty m$). In such a medium, any direction is the C_∞ axis and is perpendicular to the asymmetry plane, and any point of the medium is an inversion center. Using only symmetry considerations it is easy to determine the activity of the dipole vibrations of amorphous media (glasses and liquids) in the RS and HRS spectra.

The intensities of the dipole vibrations in the RS and HRS processes are determined by the susceptibilities of third and fourth rank, respectively. Since the isotropic medium is centrosymmetric, all the components of the third-rank tensor are equal to zero,[17] that is, the dipole vibrations in the RS spectra are always forbidden. The fourth-rank tensor is nonzero in all the media,[17] and the dipole vibrations are always active in the HRS. The same result can be obtained also by considering the properties of irreducible representations of the K_h groups (Table II),[18] from which it follows that only even representations (+) are active in the RS spectra, and only odd (−) in the HRS spectra, while in the IR spectra (i.e., dipole vibrations) only the odd triply degenerate irreducible representation $D^{(1-)}$ is active. The established exclu-

TABLE II. Correlation of the irreducible representations of the K_h group and its subgroups O_h and T_d; the last column lists the activities of the irreducible representations of the K_h group; α, β, and μ—in the RS, HRS, and IR spectra, respectively; R—rotations.

K_h	O_h	T_d	Activity
$D^{(0+)}$	A_{1g}	A_1	α
$D^{(0-)}$	A_{1u}	A_2	β
$D^{(1+)}$	F_{1g}	F_1	α, R
$D^{(1-)}$	F_{1u}	F_2	β, μ
$D^{(2+)}$	E_g+F_{2g}	$E+F_2$	α
$D^{(2-)}$	E_u+F_{2u}	$E+F_1$	β
$D^{(3+)}$	$A_{2g}+F_{1g}+F_{2g}$	$A_1+F_1+F_2$	α
$D^{(3-)}$	$A_{2u}+F_{1u}+F_{2u}$	$A_1+F_1+F_2$	β
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sion of the dipole vibrations in the RS spectra of glasses and liquid does not agree with the existing classification of the RS lines in these media. For example, it is customarily assumed that dipole vibrations are always active in RS spectra of a liquid consisting of noncentrosymmetric molecules,[7] and all types of vibrations manifest themselves in the RS spectra of glasses.[6]

Besides the forbiddenness of dipole vibrations, other peculiarities in the selection rules of vibrations appear in RS, and we shall illustrate them with two examples of the correlation of irreducible representations of the limiting group K_h and its subgroups O_h and T_d (point groups of the molecules) (Table II).[18] It can be seen from Table II that all the even representations of the centrosymmetric molecular point group O_h become active in RS, while all the odd ones in HRS. On the other hand, in a liquid consisting of non-centrosymmetric molecules (for example of symmetry T_d) (Table II), each vibration of the molecule splits into two components, of which one is active in RS and the other in HRS. As a result, more lines become allowed in the RS and HRS than predicted by the selection rules for the molecules.

2.2 Longitudinal and transverse components of dipole vibrations in the HRS spectra and their degree of depolarization

Let $\mathbf{E}_v$, $\mathbf{E}_i$, and $\mathbf{E}_s$ be the electric-field and $\mathbf{k}_v$, $\mathbf{k}_i$, and $\mathbf{k}_s$ the wave vectors of the vibrations and of the incident and scattered waves, respectively. In the scattering geometry at $\theta = 90°$ (Fig. 1a), four possibilities can be realized:

A. $\mathbf{E}_s \| \mathbf{E}_i \| x$, i.e., $j = m = n = x$. It follows then from Table I (the first column of the HRS tensor) that only one component χ_{xxxx} differs from zero, i.e., the excited vibrations are polarized along the x axis ($\mathbf{E}_v \| \mathbf{x}$). Since the wave vector $\mathbf{k}_v$ of the excited vibration lies in the yz plane (Fig. 1a), in this case $\mathbf{E}_v \perp \mathbf{k}_v$, and consequently, only TO modes can appear in the HRS spectra.

B. $\mathbf{E}_s \| z$ and $\mathbf{E}_i \| x$. The zeroth component of HRS tensor is χ_{zxxz}. Then $\mathbf{E}_v \| z$ and under these conditions the TO and LO modes are active.

C. $\mathbf{E}_s \| x$ and $\mathbf{E}_i \| y$. Only the TO modes are active (χ_{xyyx}).

D. $\mathbf{E}_s \| z$, $\mathbf{E}_i \| y$. The TO and LO modes are active (χ_{zyyz}).

Thus, in the HRS spectra at $\theta = 90°$ it is possible in principle to separate the TO and the LO vibrations with the aid of polarization measurements.

The degree of depolarization of the scattered light in the HRS process is

$$\rho = I_B/I_A,$$

where I_A and I_B are the HRS intensities in the geometries **A** and **B**, respectively. Since $I_A(LO) = 0$, it follows that $\rho(LO) = \infty$, i.e., the LO vibrations have an anomalous degree of depolarization. From Table I and Fig. 1a it follows that

$$I_A(TO) = 9(\sin\varphi)^{-2} I_B(TO) = 18 I_B(TO),$$

i.e., $\rho(TO) = \frac{1}{18}$. We note that the results obtained for the degree of depolarization are valid if the HRS tensor is symmetric with respect to the three indices j, m, and n. In the general case, when the HRS tensor is symmetric only with respect to the indices m and n, the value of ρ for the LO vibrations does not change, and for TO vibrations the degree of depolarization can differ from $\frac{1}{18}$.

We consider now the scattering geometry at $\theta = 180°$ (Fig. 1b). In this case $\mathbf{E}_i$, $\mathbf{E}_s \perp y$, and the intensity of the HRS can receive contributions from the following components (Table I): χ_{zzzz}, χ_{zxxz}, χ_{xxxx}, and χ_{xzzx}. Consequently, $\mathbf{E}_v \perp y$, i.e., $\mathbf{E}_v \perp \mathbf{k}_v$. Thus, in backward scattering only TO modes can be active in the HRS spectrum.

It is easy to show that in the case of forward scattering ($\theta = 0°$), both TO and LO vibrations can be active in the HRS spectra.

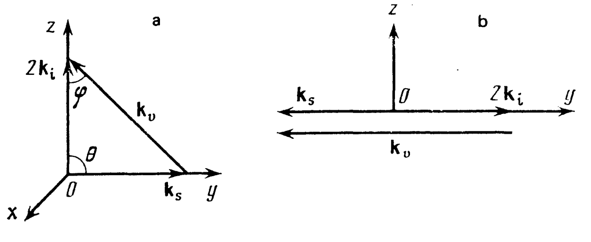

FIG. 1. Arrangement of wave vectors in the scattering geometries $\theta = 90°$ (a) and $\theta = 180°$ (b); $\mathbf{k}_i$ and $\mathbf{k}_s$ are the wave vectors of the incident and scattered light, respectively; θ is the scattering angle; φ is the angle between the wave vector $\mathbf{k}_v$ of the vibration with the z axis ($\varphi \approx 45°$ at $\theta = 90°$).

3. EXPERIMENTAL TECHNIQUE

The HRS spectra of glasses and liquids were recorded with the aid of a previously described multichannel spectrometer.[19] In the present paper, the conditions under which the HRS spectra were obtained were improved by exciting the HRS with a pulsed YAG Laser ($\omega_i = 9396\ \text{cm}^{-1}$) with continuous pumping of the active element (pump power ~ 5 kW) and with Q-switching of the cavity by an acousto-optical shutter (switching frequency 4–60 kHz). Under conditions that are optimal from the viewpoint of the intensity of the HRS signal, the repetition frequency was ~ 5 kHz, the pulse duration 100 nsec, and the peak power 20 kW. With such an excitation, the HRS intensity (the number of photons per second) was comparable with the intensity obtainable by exciting the pulses with peak power ~ 2 MW, duration 10 nsec, and repetition frequency 25 Hz. However, excitation with 20 kW pulses lowered greatly the probability of dielectric breakdown of the sample compared with the breakdown probability when megawatt pulses are used for the excitation.

To decrease the influence of the noise of the electron-optical image converter (IC), its first chamber was gated. Compared with Ref. 19, in the present study the gating frequency was increased by more than two orders. Nonetheless, even in this case the IC noise level remained the same as before, $\sim 10^{-1}$ photoelectrons per second and per resolvable element (0.1×3 mm). The reason is that at the noise density of the photocathode used in the visible region, $\sim 10^3$ photoelectrons/sec·cm^2 and off-duty cycle of the gating pulses $\sim 10^3$, the noise level from the photocathode (the first chamber of the IC) was $\sim 10^{-2}$ photoelectrons/sec per resolvable element. Thus, the IC Noise level was determined

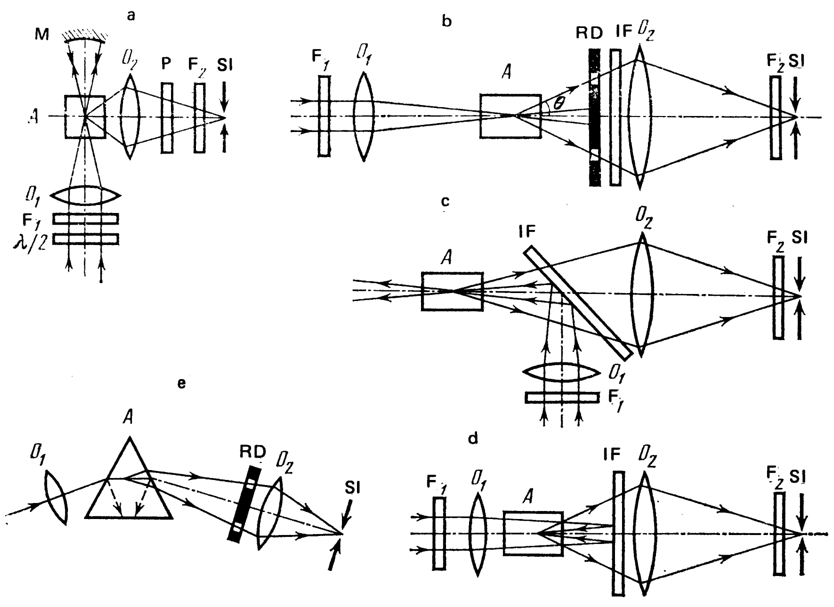

FIG. 2. Systems for observation of the HRS spectra (a–d) and RS (e) at different scattering angles θ: a) 90°; b,e) 0°; c,d) 180°; A) Sample: O_1, O_2) lenses; IF) Interference filter; P) polarizer; RD) ring diaphragm; SI) entrance slit of spectrometer; F_1) KS-19 filter; F_2) filter absorbing the laser radiation and transmiting the entire visible region of the spectrum.

principally by the properties of the second and succeeding chambers, whose operating regime remained unchanged. To gate the IC, unblocking pulses of amplitude 2 kV and flat-top duration ~ 150 nsec were applied to the shutter plates of the normally shut-off IC. To synchronize them with the laser radiation, we used a square-wave generator that controlled the shutter and, in turn, was triggered by the leading front of the modulation voltage of the acousto-optical shutter. The exact temporal coincidence of the shutter and laser pulses was achieved by regulating the delay between the pulses, which usually amounted to 1–2 μsec.

In the investigation of the HRS and RS spectra we used several systems for gathering the scattered light (Fig. 2): at an angle 90° (a), forward (b, e), and backward (c, d). The exciting radiation was focused by lens O_1, the focal length of which was 4 cm in scheme *a* and 24 cm in schemes b–e. Schemes b–d, the interference filter IF reflected totally the exciting radiation ($\omega_i = 9396$ cm^{-1}), but transmitted the HRS. Ring diaphragms RD, used for forward scattering, had a ring-gap width ~ 1 mm and were used to investigate the scattered light at a specified angle θ, which was determined by the average radius of the ring. By choosing RD with different average ring-gap radii it was possible to vary the external angle θ discretely from 0 to 10°. The distance from the RD to sample *A* was approximately 10 cm.

The investigated liquid was purified by vacuum distillations. After purification, the threshold of the dielectric breakdown of the liquid exceeded 10^9 W/cm^2, a level equal to the power density of the laser radiation in the focal region inside the sample.

In the investigation of the RS spectra in the forward geometry (scheme 2e), the scattered light was analyzed with a spectrograph with triple monochromatization, consisting of a double pre-monochromator with subtraction of the dispersion and a DFS-4 spectrograph.[20] The spectral resolution ~ 4 cm^{-1} was determined by the DFS-4 spectrograph, which was also used in the investigation of the HRS spectra.

4. EXPERIMENTAL RESULTS AND THEIR DISCUSSION

4.1. Selection rule with respect to the wave vector of vibrational excitations of glasses and liquids in HRS

When discussing the selection rules with respect to the wave vector, we use the results of experiments of three types: HRS by polaritons, polarization investigations of the HRS at $\theta = 90°$ and of HRS at $\theta = 180°$.

1. HRS *by polaritons*. We have previously reported the substantial change of the HRS spectra at small scattering angles θ in glasses and liquids compared with the spectrum at $\theta = 90°$ (Refs. 8–10). The cause of these changes is that HRS by polaritons is observed at small scattering angles. Further investigations have shown that polaritons can be observed in the spectra of all glasses. By way of example, Fig. 3 shows polaritons of the upper branch of optical glass TF-5. Observations of the dependences of the polariton frequency on the scattering angle have led us to the conclusion that the momentum-conservation law is satisfied in HRS by polaritons in glasses and liquids.[8–10] Otherwise, one would not observe in the HRS spectra a frequency dependence of the po-

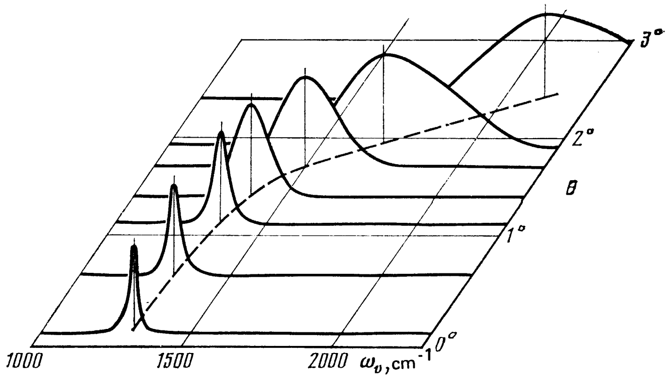

FIG. 3. HRS spectra of polaritons of the upper branch of the TF-5 glass at different scattering angle θ.

lariton on the scattering angle. The polariton, being a mixed state of electromagnetic field and transverse vibrations of ions, contains information also in the transverse mechanical vibrations of the ions. One can therefore expect the momentum conservation laws to hold also for the mechanical vibrations in glasses and in liquids (see Sec. 4.1.2).

2. *Polarization investigations and backward scattering in glasses.* It is known that vibrational excitations of purely mechanical character can be observed in large scattering angles ($\theta > 10°$). If the mechanical vibrations were describable by a definite wave vector then, according to Sec. 2.2, the bands of the *TO* and *LO* vibrations in the HRS spectra at 90° should be polarized [$\rho(TO) = \frac{1}{18}$, and $\rho(LO) = \infty$], and at $\theta = 180°$ only the *TO* modes should remain in the HRS spectrum. In addition, with decreasing scattering angle in the HRS spectrum, the *LO* modes should remain in place, while the *TO* vibrations, which turn into polaritons, should be shifted into the low-frequency region. We shall verify these singularities of the *TO* and *LO* modes using as an example HRS spectra of fused quartz (SiO_2) at $\theta = 0$, 90, and 180°.

The correspondence between the spectral bands of HRS of SiO_2 to the *TO* and *LO* modes is well known.[21] In the $\theta = 90°$ scattering geometry one observed in the HRS spectra four *TO–LO* doublets (Fig. 4a). At small scattering angles there appears in the spectra a 600–1000 cm^{-1} broad band (Fig. 4b) connected with polaritons,[8] and in addition, as expected, the *TO* modes vanish, as can be clearly seen with the 470 and 1060 cm^{-1} *TO* bands as an example.

We turn now to the polarized HRS spectra of SiO_2 (Fig. 5), obtained at $\theta = 90°$, when there are no polaritons in the spectra. In the scattering geometry $z(xxx)y$, according to Sec. 2.3, only *TO* modes should be present in the spectrum. In fact, despite the large gathering angles (~ 0.13 sr), the intense *LO* bands at 530 and 1260 cm^{-1} have vanished almost completely (Fig. 5a). This has made it possible to determine more accurately the position of the *TO* mode at 1235 cm^{-1}, which could be seen in unpolarized spectra only in the form of a weak shoulder of the 1260 cm^{-1} line (Fig. 4a).

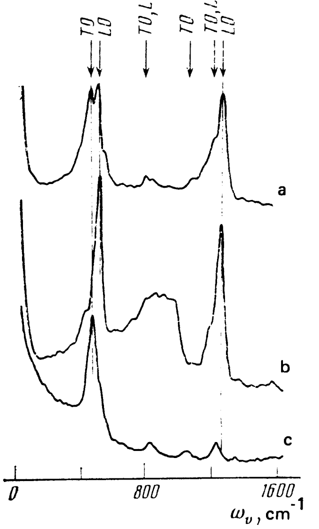

FIG. 4. HRS spectra of fused quartz at different scattering angles θ: a) 90°; b) 0°; c) 180°.

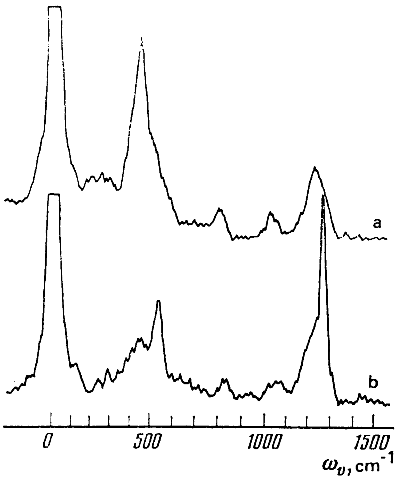

FIG. 5. Polarized spectra of HRS of fused quartz at scattering angles $\theta = 90°$: a) $z(xxx)y$; b) $z(zxx)y$. The indices z and y outside the parentheses are the directions of the incident and scattered rays, respectively (Fig. 1a); the first index in the parentheses pertains to the polarization of the scattered light ($\mathbf{E}_s$), and the two others to the polarization of the incident light ($\mathbf{E}_x$).

In the HRS spectrum at the scattering geometry $z(zxx)y$ there are present both *TO* and *LO* modes (Fig. 5b), i.e., the *LO* modes are anomalously polarized. In backward scattering ($\theta = 180°$), the 530 and 1260 cm^{-1} *LO* modes have completely vanished from the HRS spectra (Fig. 4c), and the resultant spectrum is close to that of *TO* vibrations at the scattering geometry $z(xxx)y$ (Fig. 5a).

Observation of polaritons, the polarization spectra at $\theta = 90°$, and the character of the spectrum at $\theta = 180°$ all offer evidence that the momentum conservation law is satisfied in the HRS process, i.e., the vibrational excitations (polaritons and purely mechanical vibrations) in fused quartz are characterized by a definite wave vector. This property is possessed not only by fused quartz. Figure 6 shows the HRS spectrum of glass of the system $6TiO_2$–$94SiO_2$. Its spectrum was discussed in detail in Ref. 22. Here we wish to call attention to the anomalous polarization of the bands marked by the arrows and belonging to the *LO* modes.[22]

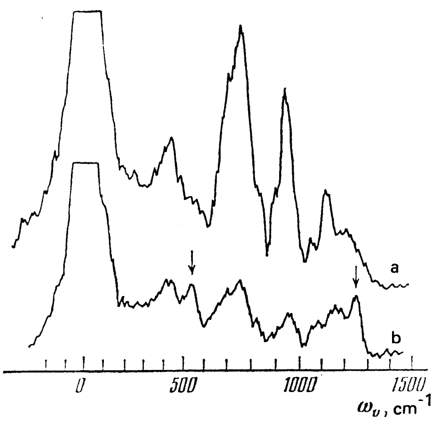

FIG. 6. Polarized spectra of HRS of $6TiO_2$–$94SiO_2$ glass: a) $z(xxx)y$; b) $z(zxx)y$; arrows indicate *LO* modes.

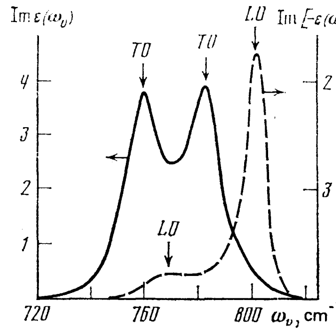

FIG. 7. Frequency dependences of the imaginary part of the dielectric constant $\mathrm{Im}\varepsilon(\omega)$ and of the loss function $\mathrm{Im}[-\varepsilon(\omega)]^{-1}$, of the liquid CCl_4, calculated from data on optical constants $\hat{n}$ taken from Ref. 24.

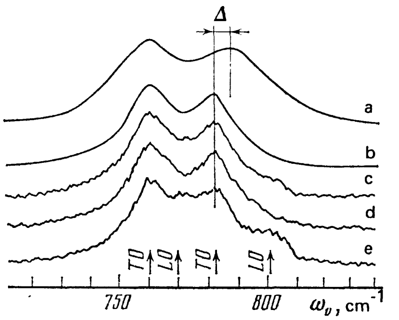

FIG. 8. RS spectra (a) and HRS spectra (b–e) of the liquid CCl_4; a) $z(xx)y$; b) $z(xxx)y$, c) $z(zxx)y$; d) $z(xyy)y$; e) $z(zyy)y$. For each of the spectra there is a separate intensity scale: Δ) disparity of the frequencies of the bands in the RS and HRS spectra.

3. *Observation of LO–TO splitting and polarization investigations of the* HRS *spectra of liquid* CCl_4. In contrast to glasses, *LO–TO* splitting of the dipole vibrations was not observed in liquids before. The observation of polaritons in CCl_4 (Ref. 10) presupposes the existence of *LO–TO* splitting, and this has stimulated searches for *TO–LO* modes in the HRS spectra of CCl_4, to be able to study subsequently their polarization properties.

It is known that the vibrational spectrum of the CCl_4 molecule contains two dipole lines that are active in the IR and in HRS: 314 cm^{-1} and a Fermi-resonant doublet near 780 cm^{-1} (Ref. 23). In the IR spectra, the intensity of the 278-cm^{-1} doublet is almost 100 times that of the 314 cm^{-1} band. Therefore the oscillator strength and the *LO–TO* splitting of the 314 cm^{-1} band should be small, as was indeed confirmed by the polariton spectra,[10] in which no gap was observed in the 314 cm^{-1} region. We therefore confine ourselves hereafter to an investigation of the spectra near 780 cm^{-1}.

Preliminary information on the *LO–TO* splitting can be obtained from an anslysis of the data on the optical constants $\hat{n} = n - i\varkappa$ for CCl_4, which are known in the 720–822 cm^{-1} region.[24] From the values of $\hat{n}$ (Ref. 24) it was possible to calculate the function $\mathrm{Im}\varepsilon(\omega_\upsilon)$ and $\mathrm{Im}[-\varepsilon(\omega_\upsilon)]^{-1}$, whose maxima were close to the position of the *TO* and *LO* modes, respectively. [$\varepsilon(\omega_\upsilon)$ is the dielectric constant]. It can be seen from Fig. 7 that in the region 720–822 cm^{-1} one expects two *TO* modes and two *LO* modes.

The HRS spectrum of CCl_4 was investigated earlier, but with poor resolution and without polarization measurements.[25,26] We investigated it at the different scattering geometries with resolution 4 cm^{-1} (Fig. 8). At the geometry $z(xxx)y$ one expects in the HRS spectra only *TO* vibrations (Sec. 2.3), but one can see in them bands at 760 and 782 cm^{-1}, which are components of the Fermi-resonance doublet (Fig. 8b). In the $z(zxx)y$ geometry, the intensity of the spectrum is decreased by a factor ~ 18, in accord with the expected decrease of the intensity of the *TO* modes (Sec. 2.3). In this geometry the *TO* and *LO* modes should be active. In addition to the *TO* bands one can see in the spectrum a weak shoulder at 800 cm^{-1} (Fig. 8a). In the two spectra considered above, the intensity of the *TO* lines is concentrated mainly in one polarization $\mathbf{E}_s \parallel x$, and this might lead to a distortion of the polarization measurements in the spectrum at $\mathbf{E}_s \parallel z$. We have therefore investigated the HRS spectra also in the geometries $z(xxx)y$ and $z(zyy)y$, at which the intensities of the *TO* lines could differ by not more than two times (Fig. 8d,e).

In the $z(zyy)y$ geometry, the 800 cm^{-1} band is seen with the best contrast (Fig. 8e), and its appearance, just as in the $z(zxx)y$ geometry, can be connected with the fact that it pertains to an *LO* vibration (item 2.3). It was more difficult to determine the position of the other *LO* vibration, which probably lands in the region between the *TO* bands at 760 and 782 cm^{-1}. This is confirmed by the spectrum of the *TO* + *LO* vibrations (Fig. 8e), in which the dip between 760 and 782 cm^{-1} bands becomes measured out, whereas in the *TO*-vibration spectrum (Fig. 8d) it is noticeably deeper. Its frequency is estimated to be close to 770 cm^{-1}.

Thus, the dipole vibrations of liquid CCl_4 are split into *TO* and *LO* components that have in the HRS spectra the same polarization properties as in the spectra of glasses. It can therefore be concluded that in liquid CCl_4, just as in glasses, the vibrational excitations are characterized by a definite wave vector. As applied to glasses, this conclusion concerns only the principal maximum of the HRS spectrum. It should be noted that the HRS spectrum of glasses, just as the RS and IR spectra, contains besides the definite albeit broad maxima also a fine-structure background, which is preserved at all scattering angles. We assume that it can be due to violation of the momentum conservation law. The intensity of the background amounted to less than 10% of the intensity of the observed bands.

We must stop to discuss the reliability of the spectra presented in the present paper. Each spectrum is the result of prolonged averaging (in the memory of the digital storage unit) of the information obtained from 10^5–$5\cdot10^6$ laser pulses, and the fact that the spectrometer (recording system) consists of many channels makes it possible to state that all the bands of each spectrum were recorded under identical conditions. Both these circumstances alter significantly the influence of static scatter of the relative intensities of the bands of the spectrum. In other words, the presence in the spectra of various details of spectra is sufficiently reliable. On the other hand, the extremely low cross section of the HRS process makes it difficult to reach a high accuracy in the measurement of the band intensities. In our case, this accuracy is sufficient at least to establish the presence or absence of various bands (Fig. 6) or the position of their maxima (Fig. 8). A quantitative estimate of the measurement accuracy of the intensities has shown that under the most unfavorable conditions the error does not exceed 30%. This is confirmed by the scatter of the intensities of the corresponding bands on different spectrograms of one and the same object.

4.2 Selection rules with respect to the matrix element in vibrational spectra of glasses and liquids

The central symmetry of the group $\infty\infty m$ presupposes exclusion of dipole vibrations in the RS spectra, as well as splitting of each vibration of a noncentrosymmetric structure element (or molecule) into two components, of which one is active in RS and the other HRS (Sec. 2.1). These peculiarities of the vibrational spectra of glasses and liquids were investigated by us with the aid of RS and HRS at small scattering angles θ, and by comparing the RS and HRS at $\theta = 90°$.

1. RS *and* HRS *spectra at small scattering angles.* If dipole vibrations could be active in RS, we could obviously observe at small scattering angles the polaritons connected with these vibrations. Figure 9 shows the dispersion relations $\omega(k)$ of the polaritons of fused quartz, as verified by the HRS spectra.[8] From the known values of the refractive indices of quartz it is possible to obtain the $\omega_\theta(k)$ dependence at $\theta = \text{const}$ (dashed-dot lines in Fig. 9) for the RS process. If the dipole vibrations were active in RS, one would observe in the RS spectra a noticeable shift of the frequencies of the transverse vibrations with decreasing scattering angle, from 1060 to 850 cm^{-1}, from 820 to 600 cm^{-1}, etc.

The setup for observing the RS at small angles is shown in Fig. 2e. It made it possible to investigate the RS spectra down to scattering angles $\theta = 0.5°$. The choice of the shape of the sample in the form of a prism and the blackening of its base (Fig. 2e) kept out of the spectrograph any stray light reflected from the front and rear faces of the sample. It was found that when the scattering angle was decreased from 90 to 0.5°, no changes whatever were observed in the RS spectra, and the spectral lines were not shifted (Fig. 9, points). A similar result was obtained also in the RS spectra of liquid CCl_4, in which the Fermi-resonance doublet 780 cm^{-1} should have shifted to 570 cm^{-1} at 0.5°, but remained in place at all scattering angles.

The absence of polaritons in the RS of glasses and liquids can be attributed to one of two possibilities: (a) the conservation law of the momentum is not satisfied, in the scattering process, but this contradicts the HRS data; (b) the dipole vibrations are not active in the RS spectra.

2. *Inequality of the frequencies in the* RS *and* HRS *spectra of glasses and liquids.* The forbiddenness of dipole vibrations in RS presupposes the absence from the RS spectra of bands pertaining to the *LO* vibrations in the HRS or IR absorption spectrum. In addition, according to Sec. 2.2, in glasses and in liquid it is presumed that the dipole vibrations of the molecules are split into two components, one of which (without the dipole) is active in the RS, and the other (*TO* vibration) in HRS. As a result, a difference could appear in the positions of the lines in the RS and HRS spectra.

A comparison of the spectra obtained by different physical methods is always difficult, since they are obtained with different instruments. When HRS spectra are excited by the fundamental harmonic, and the RS spectra by the second harmonic of the laser, we were able to obtain RS and HRS spectra with one and the same spectrometer under identical conditions and in one and the same frequency region. This has inabled us to compare directly the two types of spectra and determine the disparity Δ of the bands with acccuracy better than 1 cm^{-1} in the CCl_4 spectra and 5 cm^{-1} in the spectra of the glasses.

The RS and HRS spectra of liquid CCl_4 are shown in Fig. 8. It turned out that in these spectra the low-frequency components of the doublet (760 cm^{-1}) coincide, and the high-frequency component is located at 782 cm^{-1} in HRS at 786 cm^{-1} in RS. The HRS bands were found to be narrower than in RS, and despite the smaller distance between components the dip between them turns out to be deeper in the HRS spectrum.

Even larger discrepancies are observed in the spectra of

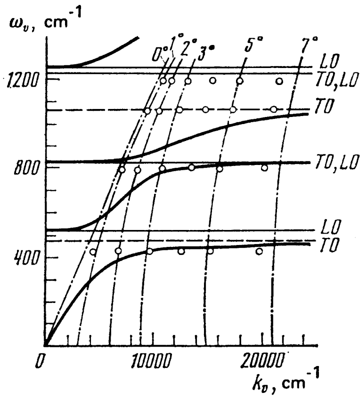

FIG. 9. Dispersion relations $\omega(k)$ of the dipole vibrations in fused quartz. Dash-dot curves—family of $\omega_\theta(k)$ curves at fixed angles θ indicated in the figure. In the calculation of $\omega_\theta(k)$ it was taken into account that the RS spectra were excited by the second harmonic of the laser and that the refractive indices are $n_i = 1.46078$, $n_s = n_i - 0.00000135\omega$. Points—measured positions of the bands at different angles.

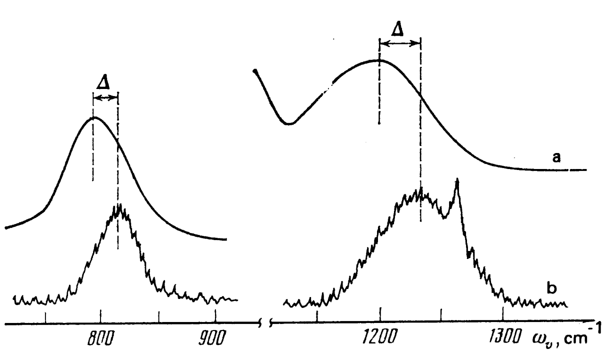

FIG. 10. RS (a) and HRS (b) spectra of fused quartz. The HRS spectrum was obtained at $z(xxx)y$ geometry, when only the *TO* modes are active. The arrow shows the 1260 cm^{-1} *LO* modes, which is intense in a different polarization of the scattered light; it appeared because of the large gathering angle of the scattered light; Δ) disparity of the maxima in the RS and HRS spectra.

fused quartz (Fig. 10). One of the most intense bands of the HRS spectra, 1260 cm^{-1}, belonging to the *LO* vibration,[21] is absent from the RS spectra. In the HRS spectra the maxima of the number of *TO*-vibration bands turned out to be shifted toward the high-frequency side by 15–30 cm^{-1} relative to the maxima in the RS spectra. The difference between the positions of the bands in the RS and HRS spectra, and the absence of *LO* vibrations in RS, agree with the expected properties of the vibrational-spectrum band (item 2.1).

The facts cited in Secs. 4.2.1 and 4.2.2 offer evidence that in the vibrational spectra of the investigated glasses and liquid there appears an mutual exclusion, according to which only dipole-less vibrations are active in the RS spectra. We emphasize that the exclusion of dipole transitions in RS is rigorous, inasmuch as it is due to the macroscopic symmetry of the anisotropic medium.

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