Spectroscopy of resonance hyper-Raman scattering of light

A. V. Baranov, Ya. S. Bobovich, and V. I. Petrov

S. I. Vavilov State Optical Institute, Leningrad
Usp. Fiz. Nauk **160**, 35–72 (October 1990)

The basic physical principles of resonance hyper-Raman scattering (RHRS) of light by media in different aggregate states are examined. The theory of RHRS by molecules, which takes into account the vibronic interaction between the resonance electronic states of a molecule, is presented. Expressions are given for the components of the tensor of RHRS in vibrational and vibrational-rotational transitions. The selection rules, the symmetry of the RHRS tensor, the polarization characteristics of the process, and the ratios of the intensities of scattering by totally and nontotally symmetric vibrations and their overtones are discussed. The results of experimental investigations of RHRS by molecules in the gas phase and molecules adsorbed on ultradispersed particles of silver are presented. These results confirm that the proposed theory adequately describes the actual process of RHRS qualitatively and in a number of cases quantitatively also, and they demonstrate that RHRS is a good source of spectral information. Data on RHRS by phonons in solids, for which there is still no theory, also show that RHRS spectroscopy could potentially yield a great deal of information.

INTRODUCTION

Hyper-Raman scattering (HRS) of light[1] by atoms, molecules, crystals, and glasses is a nonlinear three-photon energy-conversion process, in which two quanta with, in the general case, different frequencies $\hbar\omega_1 + \hbar\omega_2$ of the exciting radiation and one quantum $\hbar\omega_0$ of the scattered radiation participate. The expression $\hbar\omega_1 + \hbar\omega_2 - \hbar\omega_0$ corresponds to the difference of the energies of the initial and final states and, as a rule, is equal to the energy of the vibrational, vibrational-rotational, or purely electronic resonances. In the phenomenological description the effect is related with the hyperpolarizability by the β coefficient in the quadratic term of the expansion of the induced dipole moment in powers of the field.

The selection rules for the vibrational transitions in HRS permit observing modes that are active in the IR absorption spectra. Some other modes, which are forbidden in IR absorption and in the usual (two-photon) Raman scattering (RS), can also be allowed in HRS.[2,3] Thus HRS can be regarded as a new spectroscopic method, supplementing the traditional methods, for studying materials. This explains, in particular, the extraordinary attention that is devoted to HRS in the literature. In our country very interesting results, concerning both the properties of the effect itself and the problem of the vitrified state of matter, have been obtained in the last few years for condensed media using HRS.[4]

According to Placzek,[5] aside from the selection rules for the vibrational transitions, it makes sense to study also the rules for the intensities of vibrational transitions. For the RS spectra of transparent media it has been established that the totally symmetric vibrations usually have the highest intensity and that the overtones and the combination tones are very weak and in addition their intensity drops off rapidly as the order of the scattering increases. However the situation can sometimes change substantially already for RS excited in the characteristic absorption bands of the system (in resonance RS (RRS)). This is easy to understand based on a variant of the theory of RRS that is generally accepted and appears extensively in the literature.[6,7]

The physical idea employed in this variant of the theory consists of taking into account systematically the vibronic structure of the absorption band active in the scattering as well as the role of the vibronic interaction of the electronically excited levels with one another and with the ground state. Without going into details, for the time being, we merely note that in this case the expression for the matrix element of the polarizability decomposes into three terms (A, B, and C in the notation used in Ref. 7) which depend differently on the frequency of the exciting light. The first term describes the intensity of the totally symmetric vibrations while the second term describes the nontotally symmetric vibrations which are active in combination with the other vibrations. The third term describes the interaction of the ground state with the electronically excited states and in most cases it can be neglected. It has been found that the strongest lines appearing in RRS in the strong absorption bands are the lines of totally symmetric vibrations. The fact that the nontotally symmetric vibrations which are active in combination with other vibrations are predominantly amplified corresponds to the situation when the excitation is conducted within a weakly resolved component of a forbidden absorption band and it draws intensity from the strong band of the vibronically coupled electronic-vibrational transition.[7]

This review is devoted to resonance HRS (RHRS), which arises when the frequency of at least one of the photons ω_1 and ω_2 participating in the act of HRS or their sum frequency fall in the region of real quantum transitions characteristic for the scattering medium. This results in a sharp (by up to six orders of magnitude) intensification of the recorded signal and causes the recorded signal to depend explicitly on the properties of the excited states. The vibronic structure of the corresponding transitions can be taken into account by analogy to the RRS studied above. The vibronic theory extended to the case of RHRS is presented in Part 1 of this review. Here we included the derivation of the general expressions for the third-order-scattering tensor and for the terms describing the intensity of RHRS (the analogs of the terms A, B, and C in RRS) as well as estimates of the ratios of the intensities of the totally symmetric and nontotally symmetric vibrations as well as the fundamental vibrations and their first overtones. Special attention is devoted to some questions in the theory of vibrational-rotational RHRS,

 0038-5670/90/100812-21$01.00

which in the last few years has been studied experimentally for a number of gaseous systems. The properties of the polarization of the spectral lines of HRS and the ratios of RHRS and luminescence are studied, the selection rules are summarized, and some considerations regarding the symmetry of the scattering tensor for HRS are given.

Part 2 is devoted to a description and discussion of the experimental data on RHRS with which we are familiar. The presentation is based on the principle of the aggregate state of matter, according to which gas molecules are studied first, then molecules adsorbed on particles of colloidal silver are studied, and finally solids, represented by some bulk crystals and submicroscopic particles in a dielectric glass matrix, are studied.

Investigations of molecules adsorbed on a metal have the advantage that in this case the amplification of the signal by local surface plasmons is added to the amplification by molecular resonances. Estimates show that the amplification by local surface plasmons is at least a factor of 10^4, as a result of which in many cases it has been possible to obtain higher-order RHRS spectra, to study from the general physical and structural standpoints an extensive group of organic dyes of different classes, to demonstrate the effect of simultaneous double resonances at the fundamental and doubled frequencies of the exciting light on the intensity of RHRS, and to establish the existence of a number of supplementary effects. On the whole these experiments have made it possible to test some results of the theory.

Summarizing what we have said above, we underscore the fact that RHRS spectroscopy is extremely interesting from the fundamental standpoint because, in particular, it carries unique scientific information about the properties of the ground and electronically excited states of the system being studied. This information can be most fully extracted by measuring the RHRS excitation spectra, which is a difficult problem. From the purely applied standpoint investigations of RHRS, especially combined with IR-absorption and RRS spectra, are very valuable in connection with the problem of studying the molecular and crystalline structure of matter; this is demonstrated in several examples in this review. Admitting the possibility of RHRS in very strong light fluxes, when the spontaneous process passes into the stimulated process, some authors study the possibility of developing based on this source of coherent IR radiation.[8] Finally, as we have already mentioned, resonances increase very sharply the threshold sensitivity of the method itself; this is extremely important.

Actually, HRS signals are extremely weak. In the absence of resonances the ratio of the HRS and RS cross sections can be estimated as $(E/E_m)^2$, where E is the amplitude of the incident electric field and E_m is the strength of the microscopic electric field in the material that binds the part of the electronic subsystem whose polarizability is responsible for optical processes. According to the usual estimates $E_m \sim 10^8$ V/cm, while the intensity of the incident fields is significantly lower and is bounded by the values at which electric breakdown can occur ($E \sim 10^6$ V/cm, corresponding to radiation intensity of several GW/cm^2).

The fact that the cross sections of the HRS process in transparent media are extremely small and the difficulties arising for this reason in recording this process can be easily judged from the pioneering work performed on this subject by Terhune, Maker, and Savage[1] and other publications appearing soon after it.[9,10] For example, in Ref. 1 the HRS spectra of a number of liquids and fused quartz were excited with pulses from a Q-switched ruby laser with a peak power of about 1 MW, which is close to the conditions for electric breakdown of the samples. The HRS signals were of the order of one photocount per pulse. Later, periodic-pulse lasers of moderate power but, in turn, with a high pulse repetition frequency (up to 10 kHz), which made it much easier to perform the experiment, were used to excite the spectra. In addition, significant progress has also been made in the receiving-detecting part: systems with spectrographs, operating in combination with multichannel detectors and the corresponding electronics, have been introduced as detectors, replacing the standard spectrometers with photomultipliers to select the required section of the spectrum. An apparatus of this type is described in Refs. 11 and 12.

Thus improving the experimental apparatus already made it possible to increase significantly the strength of the HRS signal. We emphasized earlier that excitation of HRS under resonance conditions can sharply increase the cross section of the process itself. In this connection we point out that the theoretical aspect of this last problem was first studied by Akhmanov and Klyshko,[13] while the first experimental results were obtained by Polivanov and Sayakhov, who observed resonance amplification of the HRS signal in a CdS single crystal by varying the energy-gap width by heating the crystal.[14]

We felt that it would not be useful to devote a special section in this review to the experimental technique. The required information is included in the sections where specific experimental results are examined.

1. VIBRONIC THEORY IN RHRS

1.1. General expressions

As is well known, in the dipole approximation the intensity of radiation per unit time for transition from the state i into the state f of an atom or molecule is equal to[15]

$$I_{if} = \frac{4\omega_0^4}{3c^3} |\mu_{if}|^2; \tag{1.1}$$

here μ_{if} is the matrix element of the transition dipole moment between the states i and f:

$$\mu_\rho = \sum_\sigma \alpha_{\rho\sigma} E_\sigma + \sum_{\sigma,\tau} \beta_{\rho\sigma\tau} E_\sigma E_\tau + \ldots, \tag{1.2}$$

where $\alpha_{\rho\sigma}$ and $\beta_{\rho\sigma\tau}$ are the linear and quadratic polarizabilities of the system and $\rho, \sigma, \tau = x,y,z$ are the axes in the coordinate system tied to the molecule. The linear term describes the standard RS at the frequencies $\omega_0 = \omega_1 + \omega_{if}$, where $\hbar\omega_{if}$ is the energy difference $E_i - E_f$ between the states i and f.

The quantum-mechanical expression for the quadratic polarizability β (hyperpolarizability), describing the HRS process, has been derived many times by different methods.[16,17] We give this expression in the notation of Ref. 3:

$$\beta_{\rho\sigma\tau}^{if} = \frac{1}{\hbar^2} \sum_{j,k} \frac{M_\rho^{fk} M_\tau^{kj} M_\sigma^{ji}}{(\omega_{ji} - \omega_1)(\omega_{kf} - \omega_0)} + \frac{M_\rho^{fk} M_\sigma^{kj} M_\tau^{ji}}{(\omega_{ji} - \omega_2)(\omega_{kf} - \omega_0)} + \frac{M_\tau^{fk} M_\rho^{kj} M_\sigma^{ji}}{(\omega_{ji} - \omega_1)(\omega_{kf} + \omega_2)} + \frac{M_\tau^{fk} M_\sigma^{kj} M_\rho^{ji}}{(\omega_{ji} + \omega_0)(\omega_{kf} + \omega_2)} + \frac{M_\sigma^{fk} M_\rho^{kj} M_\tau^{ji}}{(\omega_{ji} - \omega_2)(\omega_{kf} + \omega_1)} + \frac{M_\sigma^{fk} M_\tau^{kj} M_\rho^{ji}}{(\omega_{ji} + \omega_0)(\omega_{kf} + \omega_1)} \Bigg], \tag{1.3}$$

where $M_\rho^{fk} = \langle f | M_\rho | k \rangle$ are the matrix elements of the projection of the dipole moment of the transition from the state k into the state f on the ρ axis. $\hat{\beta}$ is a tensor of rank three and, in the general case, it has 27 independent components. In the case important in practice $\omega_1 = \omega_2 = \omega$ the tensor is symmetric with respect to the last two indices σ and τ and has 18 independent components:[3]

$$\beta_{\rho\sigma\tau}^{nk} = \frac{2}{\hbar^2} \sum_{r,s} \left[\frac{M_\sigma^{nr} M_\rho^{rs} M_\tau^{sk}}{(\omega_{sk} - \omega - i\Gamma_{sk})(\omega_{rn} + \omega - i\Gamma_{rn})} + \frac{M_\sigma^{nr} M_\tau^{rs} M_\rho^{sk}}{(\omega_{sn} + 2\omega - i\Gamma_{sn})(\omega_{rn} + \omega - i\Gamma_{rn})} + \frac{M_\rho^{ns} M_\sigma^{sr} M_\tau^{rk}}{(\omega_{sk} - 2\omega - i\Gamma_{sk})(\omega_{rk} - \omega - i\Gamma_{rk})} \right], \quad (1.4)$$

where the indices k, n, r, and s correspond to the initial, final, and intermediate states and Γ_{ij} is the width of the transition $i \to j$.

In accordance with Eq. (1.4), in HRS two types of resonances are possible: resonances with the standard single-photon absorption (SPA) band when $\omega \approx \omega_{rk}$ and resonances with a two-photon absorption (TPA) band when $2\omega \approx \omega_{sk}$. In the first case the second term in Eq. (4) can be neglected while in the second case only the third term need be considered. The double resonance case, when both conditions are satisfied simultaneously, is also possible. In this case, as before, the last term makes the dominant contribution.

In RHRS, as compared with the nonresonant variant (HRS), the ratio of the terms in the sum (1.4) changes in favor of the transitions which are excited under resonance conditions. The intensity of RHRS becomes dependent on the vibronic structure of the states participating in the act and on their interaction with other states. We shall confine our attention to the case of scattering by the vibrational sublevels of the ground state, when the initial and final electronic states are identical.

We shall write the expression (1.4) using the adiabatic vibronic functions. We shall use the Herzberg–Teller description for the interaction of the electronic states. Then the interaction-perturbed wave function has the following form:

$$\varphi_s' = \varphi_s - \frac{1}{\hbar} \sum_{f \neq s} \sum_a \frac{V_{sf}}{\omega_{fs}} Q_a \varphi_f,$$

where φ_s is the unperturbed wave function of the state s, $\hbar\omega_{fs} = \hbar(\omega_f - \omega_s)$ is the difference of the energies of the interacting states, and the operator V describes the interaction, equal to the change produced in the potential energy by the vibrations of the nuclei,

$$V = \sum_a h_a^0 Q_a,$$

where

$$h_a^0 = \left(\frac{\partial V}{\partial Q_a} \right)_{Q_a = 0}.$$

As a result of substitutions the expression for the quadratic polarizability assumes the form[18,19]

$$(\beta_{\rho\sigma\tau})_{k'n'',k'k''} = A + B + C, \quad (1.5)$$

where

$$A = \frac{2}{\hbar^2} \sum_{rr''} \sum_{s's''} L_{s's''}(2\omega) L_{r'r''}(\omega) \times M_\rho^{k's'} M_\sigma^{s'r'} M_\tau^{r'k'} \langle n'' | s'' \rangle \langle s'' | r'' \rangle \langle r'' | k'' \rangle, \quad (1.6)$$

$$B = -\frac{2}{\hbar^2} \sum_{r',r''} \sum_{s',s''} \sum_{f \neq r,s} \sum_a L_{s's''}(2\omega) L_{r'r''}(\omega) \times \Big[M_\rho^{k's'} (h_a^0)^{s'f'} M_\sigma^{f'r'} M_\tau^{r'k'} \frac{1}{\omega_{f's'}} \langle n'' | s'' \rangle \langle s'' | Q_a | r'' \rangle \langle r'' | k'' \rangle + M_\rho^{k'f'} (h_a^0)^{f's'} M_\sigma^{s'r'} M_\tau^{r'k'} \frac{1}{\omega_{f's'}} \langle n'' | Q_a | s'' \rangle \langle s'' | r'' \rangle \langle r'' | k'' \rangle + M_\rho^{k's''} M_\sigma^{s''f''} (h_a^0)^{f'r'} M_\tau^{r'k'} \frac{1}{\omega_{f's'}} \langle n'' | s'' \rangle \langle s'' | Q_a | r'' \rangle \langle r'' | k'' \rangle + M_\rho^{k's'} M_\sigma^{s'r'} (h_a^0)^{r'f'} M_\tau^{f'k'} \frac{1}{\omega_{f'r'}} \langle n'' | s'' \rangle \langle s'' | r'' \rangle \langle r'' | Q_a | k'' \rangle \Big], \quad (1.7)$$

$$C = -\frac{2}{\hbar^2} \sum_{r',r''} \sum_{s',s''} \sum_{t \neq k} \sum_a L_{s',s''}(2\omega) L_{r',r''}(\omega) \times \Big[(h_a^0)^{k't'} M_\rho^{t's'} M_\sigma^{s'r'} M_\tau^{r'k'} \frac{1}{\omega_{t'k'}} \langle n'' | Q_a | s'' \rangle \langle s'' | r'' \rangle \langle r'' | k'' \rangle + M_\rho^{k's''} M_\sigma^{s'r'} M_\tau^{r't'} (h_a^0)^{t'k'} \frac{1}{\omega_{t'k'}} \langle n'' | s'' \rangle \langle s'' | r'' \rangle \langle r'' | Q_a | k'' \rangle \Big], \quad (1.8)$$

where i' and i'' are the indices of the electronic and vibrational wave functions of the ith state, respectively, $L_{s's''}(2\omega) = (\omega_{s's'',k'k''} - 2\omega - i\Gamma_{sk})^{-1}$, and $L_{r'r''}(\omega) = (\omega_{r'r'',k'k''} - \omega - i\Gamma_{rk})^{-1}$.

The terms A, B, and C appearing in Eq. (1.5) are completely analogous to the corresponding terms in the vibronic theory of RRS[6,7,20–22] and they represent the contribution of the vibrational structure of the active SPA and TPA bands (the term A) to the intensity of the spectral lines as well as the role of the interaction of the electronically excited states with one another (the term B) and with the ground state (the term C).

Far from resonances the expressions (1.6)–(1.8) permit some approximation. Neglecting the widths of the transitions and using the fact that in the linear approximation[20,21]

$$L_{s's''}(2\omega) \approx \frac{1}{\omega_{s'k'} - 2\omega} \left(1 - \frac{\omega_{s's''} - \omega_{s'0}}{\omega_{s'k'} - 2\omega} \right),$$

$$L_{r'r''}(\omega) \approx \frac{1}{\omega_{r'k'} - \omega} \left(1 - \frac{\omega_{r'r''} - \omega_{r'0}}{\omega_{r'k'} - \omega} \right),$$

after summing over s'' and r'' we obtain that the term A becomes

$$A' = \frac{2}{\hbar^2} \sum_{r',s'} \frac{M_\rho^{k's'} M_\sigma^{s'r'} M_\tau^{r'k'}}{(\omega_{s'k'} - 2\omega)(\omega_{r'k'} - \omega)} \delta_{n''k'} - \frac{2}{\hbar^2} \sum_{r',s'} \sum_a \frac{M_\rho^{k's'} M_\rho^{s'r'} M_\tau^{r'k'}}{(\omega_{s'k'} - 2\omega)(\omega_{r'k'} - \omega)} \times \left[\frac{(h_a^0)^{s's'}}{\omega_{s'k'} - 2\omega} + \frac{(h_a^0)^{r'r'}}{\omega_{r'k'} - \omega} \right] \langle n'' | Q_a | k'' \rangle, \quad (1.9)$$

and the term B becomes

$$B' = -\frac{2}{\hbar^2} \sum_{r',s',f'} \sum_a \frac{\langle n'' | Q_a | k'' \rangle}{(\omega_{s'k'} - 2\omega)(\omega_{r'k'} - \omega)} \times \left\{ \frac{1}{\omega_{f's'}} [M_\rho^{k's'} (h_a^0)^{s'f'} M_\sigma^{f'r'} M_\tau^{r'k'} + M_\rho^{k'f'} (h_a^0)^{f's'} M_\sigma^{s'r'} M_\tau^{r'k'}] + \frac{1}{\omega_{f'r'}} [M_\rho^{k's'} M_\sigma^{s'f'} (h_a^0)^{f'r'} M_\tau^{r'k'} + M_\rho^{k's'} M_\sigma^{s'r'} (h_a^0)^{r'f'} M_\tau^{f'k'}] \right\}. \quad (1.10)$$

The first term in Eq. (1.9) is important only in the hyper-Rayleigh scattering. The second and third terms are proportional to the matrix elements of the interaction operator $(h_a^0)^{s's''} = K_a^{s'}\Delta_a^{s'}$ and $(h_a^0)^{r'r''} = K_a^{r'}\Delta_a^{r'}$, where K and Δ are the force constant and the change in the potential function in the corresponding electronic states. Since for nontotally symmetric vibrations $\Delta = 0$, Eq. (1.9) represents the predominant amplification of totally symmetric vibrations as resonance is approached $\omega \to \omega_{rk}$ and $2\omega \to \omega_{sk}$.

The following conclusions can be drawn from the foregoing analysis. When the frequency of the incident radiation approaches the frequency of the strong SPA or TPA band with a relatively large cross section the amplification is determined predominantly by the term A, which has a sharp frequency dependence, for totally symmetric vibrations. If resonance with a weak SPA or TPA band lying near a strong band is realized, the contribution of the term A to the scattering can be small compared with the term B, which describes the amplification of nontotally symmetric vibrations that are active in combination with other vibrations. Thus the RHRS spectra excited in relatively weak and relatively strong bands can have a quite different collection of vibrations.

1.2. Selection rules for HRS

The selection rules are somewhat different for HRS tensors that are symmetric with respect to all three indices, when there are only ten independent components, that are symmetric with respect to the last two indices, and that are unsymmetric.[2,3] We shall summarize the relevant results.

1. All vibrations active in IR absorption are allowed in HRS also.

2. Only odd vibrations can be active in centrosymmetric molecules, i.e., the alternative forbiddance holds in RS and HRS.

3. Vibrations that are forbidden in RS and IR absorption simultaneously ("silent modes") can be active in HRS.

4. For noncentrosymmetric molecules some types of vibrations are active in RS and HRS, simultaneously. However some vibrations are allowed in HRS but forbidden in RS and vice versa.

5. A number of vibrations, which are allowed for a tensor of general form, are forbidden in the case of tensors that are symmetric with respect to the last two and all three indices; a number of vibrations that are allowed for a tensor that is symmetric with respect to the last two indices are forbidden in the case of a totally symmetric tensor.

6. In HRS by noncentrosymmetric molecules, apart from vibrations that are active in IR absorption, other types of vibrations that are forbidden in IR absorption are allowed.

7. In centrosymmetric media, apart from dipole vibrations, other types of vibrations that are forbidden in IR absorption are allowed.

Some of the foregoing selection rules may not hold, if the symmetry of the molecules in the excited electronic states is different.[19] Using the method of Ref. 23, it can be easily shown that for molecular groups having only one-dimensional irreducible representations vibrations which contain in the decomposition of the product $T_{\rho\sigma\tau}(G_0)\times\Gamma_{H_r}(G_0)\times\Gamma_{H_s}(G_0)$ in terms of the irreducible representations of the symmetry group of the molecule in the ground state G_0 are allowed in HRS. Here $T_{\rho\sigma\tau}$ is the tensor representation and $\Gamma_{H_{r,s}}$ is the reducible, in the general case, representation of the vibrational Hamiltonian. In particular, if in the excited states the molecule loses its center of inversion, then even vibrations are also active in HRS.

In the case when the frequency, form, and symmetry of the vibrations remain unchanged in the excited states, only transitions in which the vibrational quantum number changes by one are allowed in the harmonic approximation. From Ref. 6 we have

$$\begin{aligned}\langle n''|Q_a|k''\rangle &= 0, && \text{if } v_{n''} \neq v_{k''} \pm 1,\\ &= \left[\frac{\hbar}{2\omega_a}(v_{k''}+1)\right]^{1/2}, && \text{if } v_{n''} = v_{k''}+1,\\ &= \left(\frac{\hbar}{2\omega_a}v_{k''}\right)^{1/2}, && \text{if } v_{n''} = v_{k''}-1,\end{aligned}$$

where $v_{k''}$ and $v_{n''}$ are the vibrational quantum numbers of the initial and final states, respectively, and ω_a is the vibrational frequency.

Overtones and combination tones can appear as a result of the separate or combined effect of mechanical and electrooptic anharmonicities. If the frequencies of the vibrations in the ground and excited states are somewhat different, the second-order spectrum can already appear in the harmonic approximation. For overtones, for example, in this case there arises a term of the form

$$A'' = -\frac{1}{\hbar^3}\sum_{r',s'}\sum_a \frac{M_\rho^{k's'}M_\sigma^{s'r'}M_\tau^{r'k'}}{(\omega_{s'k'}-2\omega)(\omega_{r'k'}-\omega)} \times\left(\frac{K_a^{s'}-K_a^{k'}}{\omega_{s'k'}-2\omega}+\frac{K_a^{r'}-K_a^{k'}}{\omega_{r'k'}-\omega}\right)\langle n''|Q_a^2|k''\rangle, \qquad (1.11)$$

where $K_a^{i'}$ is the force constant of the vibration a in the state i'. The selection rules for the overtones in this situation are

$$v_{n''} = v_{k''} \pm 2.$$

1.3. The ratio of the intensities of totally symmetric, nontotally symmetric, and overtone vibrations in HRS

As follows from Eqs. (1.9) and (1.10), the intensity of the spectral lines of HRS depends on the TPA cross sections for the transitions into the corresponding active states. Single-photon absorption contributes to the resonance enhancement of the TPA cross sections. The ratio of the intensities of the lines of totally symmetric and nontotally symmetric vibrations (we omit the summation signs in Eqs. (1.9) and (1.10)) is equal to

$$\frac{I_{\rm TS}}{I_{\rm NTS}} = \left|\frac{A'}{B'}\right|^2 = \left(\frac{\omega_{s's''}-\omega_{s'0}}{\omega_{s'k'}-2\omega}\right)^2\frac{\sigma_{sk}^{\rm TPA}}{\sigma_{fk}^{\rm TPA}}\left[\frac{2\Delta^{s'}}{(Q_a)_{01}}\right]^2. \qquad (1.12)$$

The first factor in Eq. (1.12) under nonresonant conditions is of the order of 10^{-3}, but its value increases as $2\omega \to \omega_{s'k'}$; this reflects the fact that it is the increase in the intensity of the totally symmetric vibrations that predominates as a strong active TPA band is approached. The number of substances for which the TPA cross sections are known is small.[24,25] Nonetheless the existing data are sufficient to estimate the second factor, which is of the order of 10^3. Finally, the third factor, according to Ref. 20, is of the order of ten, which gives the estimate $(A/B)^2 \leqslant 10$.

The ratio of the intensity of the overtone arising owing to the change in the frequency of vibrations in the excited state to the intensity of the fundamental tone can be estimated, using Eqs. (1.9) and (1.10), as

$$\frac{I_{\text{over}}}{I_{\text{fund}}} = \left[\frac{(\omega_a^{s'})^2 - (\omega_a^{k'})^2}{2(\omega_a^{s'})^2 \Delta_a^{s'}} \frac{(Q_a^2)_{20}}{(Q_a)_{10}}\right]^2 \approx \left(\frac{\Delta\omega_a}{\omega_a}\right)^2 \left[\frac{(Q_a^2)_{20}}{\Delta_a^{s'}(Q_a)_{10}}\right]^2. \tag{1.13}$$

Since usually $\Delta\omega_a/\omega_a \sim 10^{-1}$ and the second factor is of the order of 10^{-1}–10^{-2}, the ratio sought does not exceed 10^{-3}–10^{-4}.

It should be expected that at resonance the overtones and combination tones should be intensified owing to the effect of only the electrooptic anharmonicity. For a fully symmetric vibration we have

$$\frac{I_{\text{over}}}{I_{\text{fund}}} \approx \left[\frac{K_a^{s'}(\Delta_a^{s'})^2}{\hbar(\omega_{f'k'} - 2\omega)}\right]^2 \left[\frac{(Q_a^2)_{20}}{\Delta_a^{s'}(Q_a)_{10}}\right]^2. \tag{1.14}$$

Off resonance this ratio is equal to 10^{-4}–10^{-5}, but it increases rapidly as a strong TPA band is approached. Since the denominator in the first factor in Eq. (1.13) is bounded by the half-width of the electronic transition $\Gamma_{sk} \sim 10^3$ cm^{-1}, for frequencies $\omega_a \simeq 10^3$ cm^{-1} the ratio of the line intensities for scattering of second and first orders in 10^{-1}–10^{-2}. If a relatively weak TPA band vibronically coupled with a strong band is active in scattering, then the combination tones formed by a combination of the totally symmetric and nontotally symmetric vibrations which are active together with other vibrations will be strongest. The expression

$$B'' = \frac{2}{\hbar^3} \sum_{r',s',f'} \sum_{a,b} \frac{M_\rho^{k's'} (h_a^0)^{s's'} (h_b^0)^{s'f'} M_\sigma^{f'r'} M_\tau^{r'k'}}{(\omega_{s'k'} - 2\omega)^2 (\omega_{r'k'} - \omega)} \frac{1}{\omega_{f's'}} \langle n'' | Q_a Q_b | k'' \rangle, \tag{1.15}$$

which has a sharper frequency dependence than the fundamental tones of nontotally symmetric vibrations (1.10), will be responsible for their appearance. As a result, the estimate (1.14), where the corresponding factor from Eq. (1.15) should be used instead of $(Q^2)_{20}$, will remain valid for the intensity of the combination tones.

1.4. Symmetry of the HRS tensor

Investigation of the symmetry of the RS tensor revealed that far from the electronic and vibrational absorption bands of the system and in the absence of degeneracy of the ground electronic state (Placzek's condition) the scattering tensor is, with a high degree of accuracy, symmetric.[5] The ratio of the antisymmetric and symmetric parts of the tensor gives a quantitative measure of asymmetry. The following estimate of this ratio is given in Ref. 20:

$$q \approx \frac{\hbar\omega/E_0^j}{1 - (\hbar\omega/E_0^j)} \frac{\hbar\omega_a}{E_0^j}, \tag{1.16}$$

where E_0^j and $\hbar\omega_a$ are the energies of the electronic and vibrational transitions, respectively. This estimate shows that in the case under study (RS) antisymmetry can be significant only near or in the electronic absorption bands, while in the region where the substance is transparent the asymmetry can be neglected. Physically this is connected with the fact that in the zeroth-order approximation the RS tensor is symmetric and its asymmetry is connected with the fact that the vibrational structure of the excited electronic state is taken into account and it is large when it is necessary to do so, i.e., when the RS spectra are excited under resonance conditions.

The HRS tensor (1.3) and (1.4) is, as one can easily see, asymmetric already in the zeroth-order approximation (neglecting the vibronic structure of the excited electronic states). Thus the asymmetry of the HRS tensor should be observed under a wide range of excitation conditions, including also the region when the substance is transparent, and the Placzek region should be absent for most compounds. A quantitative criterion for this situation is given in Ref. 3, where it is shown that the HRS tensor becomes symmetric when the conditions $\hbar\omega/E_0^j$, $\hbar(2\omega \pm \omega_a)/E_0^j \ll 1$, are satisfied; but only the condition $\hbar\omega/E_0^j$, $\hbar(2\omega \pm \omega_a)/E_0^j < 1$ is realizable in practice. The antisymmetry of the HRS tensor has been observed experimentally in crystalline quartz[26] for excitation of the spectrum in the region of transparency, where $\hbar(\omega_1 + \omega_2)/E_0^j \sim 0.3$, and in addition it was shown that the symmetric and antisymmetric parts are of comparable magnitude. On the other hand the HRS tensor satisfies Kleinman's conditions, i.e., it is symmetric with respect to all indices. Here there is some analogy with the electronic RS, whose scattering tensor usually has a significant antisymmetric part, while the Rayleigh scattering tensor is symmetric.[27]

1.5. The degree of depolarization of spectral lines

For systems whose elements are oriented randomly relative to a stationary (laboratory) coordinate system it is impossible to measure the components of the HRS tensor separately. It is shown in Ref. 2 that for a totally symmetric HRS tensor, after the intensity of the scattered light from all molecules is averaged over the orientations of the molecules, it is possible to separate two parameters A^2 and B^2, the first of which is called the symmetric part of the quadratic polarizability and has the form

$$A^2 = \sum_{i,j,k = \text{cycle}} (\beta_{iii} + \beta_{ijj} + \beta_{kki}),$$

while the second one is given by

$$B^2 = \sum_i \beta_{iii}^2 - \frac{2}{3} \sum_{i \neq j} \beta_{iii} \cdot \beta_{ijj} + \frac{11}{3} \sum_{i \neq j} \beta_{iij}. \tag{1.17}$$

For naturally polarized incident radiation the following expression for the degree of depolarization is obtained when the scattered signal is observed at a right angle:

$$\rho' = \frac{4B^2}{7A^2 + 5B^2} \tag{1.18}$$

(for linearly polarized incident radiation $\rho = \rho'/(2 - \rho')$). From here it follows that the quantity ρ' is bounded by 4/5 ($\rho \leqslant 2/3$). In the general case, when the tensor is symmetric only with respect to the last two indices, it is possible to separate from it six invariants which transform as spherical functions, and in addition one of them is manifested only when the incident radiation is elliptically polarized.[28] As shown in Refs. 16 and 28, a symmetric HRS tensor can be described by two of these invariants, while the remaining invariants correspond to an asymmetric tensor. Kozierowski *et al.*[29] examined the case when a vibrational line that is

forbidden in IR absorption but allowed in HRS (for example, a vibrational line corresponding to the symmetry a_1'' in a molecule with D_{3h} symmetry) has, owing to the asymmetry of the tensor, a degree of depolarization equal to that in the case of excitation with linearly polarized radiation ∞ (4 and 8/3 for circularly and naturally polarized light, respectively, for observations at 90°).

In the case of vibrational-rotational HRS the degree of depolarization, taking into account the asymmetry of the tensor for excitation of the spectrum with linearly polarized radiation, is equal to[28] (for observations at 90°)

$$D_\rho = \frac{1}{9}\,\frac{7\,|\widetilde{B}_\rho^{1(1)} + \sqrt{5}\,\widetilde{B}_\rho^{2(1)}|^2 + 21\,|\widetilde{B}_\rho^{2(2)}|^2 + 12\,|\widetilde{B}_\rho^{1(3)}|^2}{7\,|\widetilde{B}_\rho^{1(1)}|^2 + 2\,|\widetilde{B}_\rho^{1(3)}|^2}, \quad (1.19)$$

where

$$|\widetilde{B}_\rho^{s(l)}|^2 = \sum_\lambda |\widetilde{B}_{\rho\lambda}^{s(l)}|^2, \quad |\widetilde{B}_{\rho\lambda}^{s(l)}|^2 = \left|\left(\frac{\partial \widetilde{B}_\lambda^{s(l)}}{\partial Q_\rho}\right)\right|^2,$$

$\rho = 1,\ldots,3p-6$, and p is the number of normal vibrations; $|\widetilde{B}_{\rho\lambda}^{s(l)}|^2 = |\widetilde{B}_\lambda^{s(l)}(°)|^2$ for $\rho = 0$; and,

$$B_\lambda^{s(l)} = \sum_{i,j,k} C_{ijk}^{sl\lambda}\beta_{ijk},$$

where the coefficients $C_{ijk}^{sl\lambda}$ are tabulated in Refs. 28 and 30 and β_{ijk} is the HRS tensor. The expression for the inversion coefficient has the form

$$R_\rho = \frac{45\,|\widetilde{B}_\rho^{1(3)}|^2}{3\,|\widetilde{B}_\rho^{1(3)}|^2 + 21\,|\widetilde{B}_\rho^{2(2)}|^2 + 28\,|\widetilde{B}_\rho^{1(1)} - (\sqrt{5}/2)\,\widetilde{B}_\rho^{2(1)}|^2}. \quad (1.20)$$

For symmetric scattering, described only by the invariants $\widetilde{B}_\rho^{1(1)}$ and $\widetilde{B}_\rho^{1(3)}$, the degree of depolarization D_ρ falls within the limits $1/9 \leqslant D_\rho \leqslant 2/3$. The degree of depolarization of hyper-Rayleigh scattering also falls within these limits.[30] The measured value of D_ρ in vibrational-rotational RHRS by NH_3 molecules is equal to 0.78,[30] indicating that the tensor responsible for RHRS is asymmetric.

1.6. Ratio of the intensities of the vibrational-rotational components of HRS

The theory of rotational and vibrational-rotational HRS is given in Refs. 28 and 31 for the symmetric and in Ref. 32 for the asymmetric HRS tensor. The rotational Hamiltonian in the coordinate system of the molecule can be written in the form

$$H_R = AJ_{x'}^2 + BJ_{y'}^2 + CJ_{z'}^2, \quad (1.21)$$

where $A = (1/2)I_{x'}^{-1}$, $B = (1/2)I_{y'}$, $C = (1/2)I_{z'}$, and I_i is the projection of the moment of inertia on the ith axis. The rotational wave functions have the form

$$|JKM\rangle = i^{J-K}\left(\frac{2J+1}{8\pi^2}\right)^{1/2} D_{KM}^J(\Omega), \quad (1.22)$$

where the quantum numbers J, K, and M are the eigenvalues of the operator $\mathbf{J}^2$ and its projection on the z' axis of the coordinate system of the molecule and the z axis of the laboratory coordinate system:

$$\begin{aligned} &\mathbf{J}^2|JKM\rangle = J(J+1)\,|JKM\rangle,\\ &J_{z'}|JKM\rangle = K|JKM\rangle,\\ &J_z|JKM\rangle = M|JKM\rangle, \end{aligned} \quad (1.23)$$

D_{KM}^J are Wigner's matrices, and $\Omega = \alpha, \beta$, and γ are Euler's angles. The eigenvalues of the operator H_R for spherical-top molecules $(2J+1)^2$ are degenerate and can be written in the following general form

$$E_R = E_J = AJ(J+1). \quad (1.24)$$

For a symmetric top

$$E_R = E_{JK} = BJ(J+1) + (A-B)K^2 \quad (1.25)$$

with degeneracy $2J(J+1)$.

We shall give the expressions for the intensity of the lines of vibrational-rotational HRS for symmetric-top molecules for linearly polarized incident radiation and observations performed at 90°:[31]

$$I \sim \frac{1}{9}|\beta^{1,2}|^2 + \frac{2}{9}|\beta^{1,0}|^2 + \frac{1}{15}|\beta^{2,2}|^2 + \frac{2}{21}|\beta^{3,2}|^2 + \frac{2}{9\sqrt{5}}\,\mathrm{Re}\,(\beta^{1,2}\beta^{1,0*}), \quad (1.26)$$

where

$$\begin{aligned} |\beta^{l,Q}|^2 = \sum_{J_1''J_2'',K_2''K_1''} &(-1)^{-J_2''-J_1''-K_2''-K_1''}(2Q+1)(2l+1)\\ &\times(2J+1)(2J_1''+1)(2J_2''+1)(2J'''+1)\\ &\times\begin{Bmatrix} l & J & J''' \\ J_1'' & 1 & Q \end{Bmatrix}\begin{Bmatrix} l & J & J''' \\ J_2'' & 1 & Q \end{Bmatrix}\begin{pmatrix} J_1'' & Q & J \\ -K_1'' & -q & K \end{pmatrix}\\ &\times\begin{pmatrix} J_2'' & Q & J \\ -K_2'' & -q & K \end{pmatrix}\begin{pmatrix} J''' & 1 & J_1'' \\ -K''' & p'' & K_1'' \end{pmatrix}\begin{pmatrix} J''' & 1 & J_2'' \\ -K''' & p'' & K_2'' \end{pmatrix}\\ &\times\left|\sum_{s,v',p,p'} \frac{(M_{p''})_{ev''}^{gv'''}(M_p)_{sv'}^{ev''}(M_p)_{gv}^{sv'}}{\omega_{gv,sv'} - \omega}\begin{pmatrix} 1 & 1 & Q \\ p' & p & q \end{pmatrix}\right|^2\\ &\times(\omega_{gv,ev''} + \omega_{JK,J_1''K_1''} - 2\omega - i\Gamma_{ev''}^{J_1''K_1''}/2)^{-1}\\ &\times(\omega_{gv,ev''} + \omega_{JK,J_2''K_2''} - 2\omega - i\Gamma_{ev''}^{J_2''K_2''}/2)^{-1}. \end{aligned} \quad (1.27)$$

The summation is performed over the rotational quantum numbers J_1'', J_2'', K_1'', K_2'', of the intermediate state, and the numbers J, K, and J''', K''' refer to the initial and final states. The indices p, p', and p'' enumerate the axes of the coordinate system of the molecule, $|gv'\rangle$ and $|gv''\rangle$ are the vibronic wave functions of the initial and final states, and $|sv'\rangle$ and $|ev''\rangle$ are the vibronic wave functions of the intermediate states. Here the indices 1 and 2 emphasize the possible contribution of cross terms in the summation over the rotational sublevels to the intensity of HRS.

An expression for the relative intensities of the vibrational-rotational components of HRS for asymmetric-top molecules is presented in Ref. 32.

The selection rules for transitions between the rotational sublevels can be derived from Eq. (1.27). The requirement that the $3j$ and $6j$ symbols appearing in Eq. (1.27) be different from zero gives $\Delta J = J''' - J = -3, -2, -1, 0, 1, 2, 3$ and $\Delta k = k'' - k = p + p' + p''$. In spectroscopy these transitions are denoted as N, O, P, Q, R, S, and T.

1.7. Ratio of RHRS and luminescence. Classification of the types of secondary luminescence

As follows from Eq. (1.3), at least four levels operate in the HRS process: initial, final, and two intermediate. The HRS cross section depends not only on the magnitude of the transition dipole moments between them but also on their vibronic interaction operators as well as their relaxational

characteristics. The latter are most strongly manifested in the conditions of resonance excitation of HRS, for example, when $\omega_1 + \omega_2 = \omega_{ik}$. In this case, together with RHRS, other processes, including also two-photon absorption $i \to k$ with actual filling of this level followed by nonradiative or radiative decay of the level to lower lying levels, are possible depending on the properties of the state $|k\rangle$. The radiative process (luminescence accompanying two-photon excitation) can occur to the same states as RHRS. In this connection there arises the problem of separating these two types of secondary luminescence and observing their relative contributions to the signal.

This problem arose earlier in application to the case of the standard RRS and single-photon luminescence. Important results in this direction were obtained in a theoretical study of three-level systems with amplitude and phase relaxations, characterizing a resonance transition.[33,34] It was shown that the absorption and subsequent photoluminescence in such systems arise only when phase relaxation is taken into account. In the case when the phase relaxation is exponential (T_2 process) the ratio of the intensities of RS and photoluminescence is equal to the ratio of the rates of amplitude and phase relaxations and does not depend on the frequency of the exciting light. As established in Ref. 34, the relative contribution of RS (I_{RS}) to the total secondary luminescence $I_0 = I_{RS} + I_{PL}$, where I_{PL} is the integrated intensity of photoluminescence, is given by the expression

$$\frac{I_{RS}}{I_0} = \frac{\gamma\,|\langle p\rangle|^2}{2\,\mathrm{Re}\,\langle p\rangle}, \tag{1.28}$$

where γ is the rate of decay of the population of the resonance level $|k\rangle$, taking into account both radiative and nonradiative transitions,

$$\langle p\rangle = \int_0^\infty f(\tau)\exp\left[i(\omega_{ik}-\omega)\tau - \frac{\gamma}{2}\tau\right]d\tau,$$

$$f(\tau) = \left\langle \exp\left(i\int_0^\tau \omega(x)\,dx\right)\right\rangle,$$

and $\omega(t)$ is the change in the transition frequency ω_{ik} owing to interaction with the environment and is a random stationary quantity with zero mean ($\langle\omega(t)\rangle = 0$). The ratio I_{RS}/I_0 was calculated in Ref. 34, under the assumption that $\omega(t)$ is a Gaussian random function whose correlation function is equal to $\langle\omega(0)\omega(t)\rangle = \Delta^2\exp(-t/\tau_m)$, where $\Delta^2 = \langle\omega^2(t)\rangle$ and τ_m is the correlation time. It was found that I_{RS}/I_0 depends on the frequency, and in addition it approaches unity as the distance from resonance increases. The rate of phase relaxation $\gamma_{ph} = 1/(2T_2)$ can be derived for δ-correlated modulation $\omega(t)$. Then $f(\tau) = \exp(-\gamma_{ph}\tau)$, and

$$\frac{I_{RS}}{I_0} = \frac{\gamma}{2\gamma_{ph} + \gamma}$$

does not depend on the frequency.

In Refs. 33 and 34 it was also shown that the width of the components of the secondary resonance emissions are determined by different constants and can be different. If the spectral widths of the source of excitation and of the final state can be neglected, then the spectral width of the RS line can be represented by a δ function, and the spectral width of the luminescence band can be represented by the total width of the resonance state. For this reason, in the limit when the width of the intermediate state is large both components of the secondary luminescence can be easily discriminated spectrally. When RS is excited by pulses of light whose width is less than the lifetime of the resonance state the RS and luminescence can be resolved in time: the first type of emission is excited only at the moment the pulse acts while the second type relaxes exponentially at a rate inversely proportional to the lifetime of the excited state.[33]

It is obvious that all the characteristics enumerated above are also true for RHRS and two-photon luminescence. Investigations of the profiles of excitation of RRS and RHRS of vibrational-rotational transitions in gaseous ammonium[35] showed that the spectral widths of the resonance intermediate states are much greater than those of the individual secondary luminescence bands, and from here it was concluded that these bands belong to scattering and not photoluminescence. In the case when the intermediate state is not broadened much, time-resolved measurements could be useful for identifying the type of secondary luminescence.[36]

2. DESCRIPTION, DISCUSSION, AND INTERPRETATION OF THE EXPERIMENTAL RESULTS ON RHRS

2.1. Vibrational-rotational transitions in gases

The advantage of simple molecular gases as objects for investigating RHRS at low and moderate pressures over most other systems is that their characteristic vibronic transitions are narrow. This makes it possible to obtain large spectral resonance enhancement factors. On the other hand, however, under such circumstances there arises the new problem of identifying the true type of secondary luminescence, i.e., the problem of distinguishing RHRS from luminescence. Some theoretical considerations regarding this problem were given in Sec. 1.7. In practice the matter is closed when nonradiative deactivation of the resonance state, occurring at rates at least an order of magnitude higher than the rate of vibrational relaxation in the ground state, occurs.

Precisely this case was realized in Ref. 35 and in the subsequent series of very interesting publications by the same group[31,37–39] on the first reliable observation of RHRS spectra on vibrational-rotational (VR) transitions of NH_3 and ND_3 molecules under the conditions of two-photon resonance of the exciting radiation with the v_2'' band of the transition ${}^1A_1' - {}^1A_2''$. The resonance state ${}^1A_2''$ is a predissociation state, and when the molecule is excited into this state it dissociates with unit quantum yield ($NH_3 \to NH_2 + H$). It was shown earlier[39] that the width of the rotational-vibronic (RV) levels of the ${}^1A_2''$ state ($\sim 60\ \mathrm{cm}^{-1}$) are entirely determined by this process, and in Ref. 35 it was established that the contribution of luminescence to the secondary luminescence of the molecules excited by means of two-photon absorption is negligibly small. In this sense the situation in other molecules (CH_3I and CS_2), for which a discrete spectrum of secondary luminescence in the gas phase under conditions of two-photon absorption was also obtained,[37] is ambiguous, since in spite of the fact that even here the resonance state is a predissociation state, the width of the RV levels of this state is comparable to the observed width of the spectral lines of the secondary luminescence (5–10

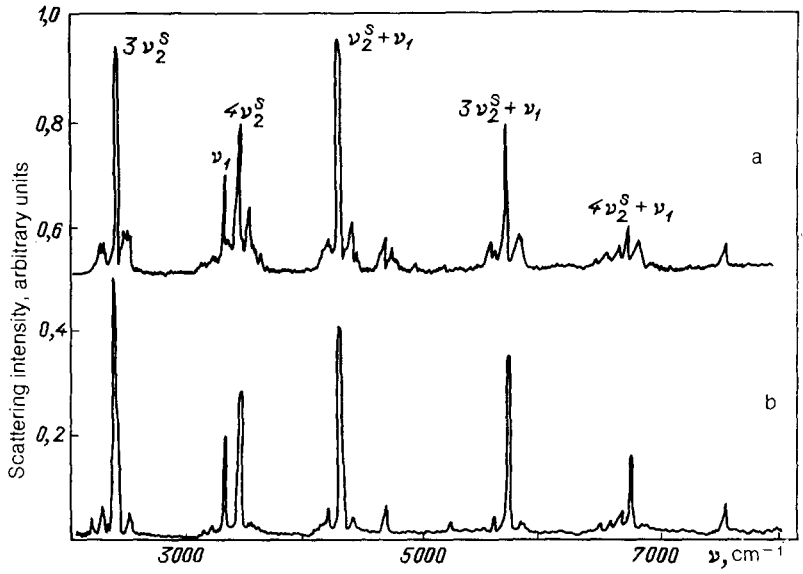


FIG. 1. a–The RHRS spectrum of NH_3 (8 atm) with excitation at 417.6 nm. b–RRS spectrum of NH_3 (20 Torr) with excitation at 208.8 nm.[37]

cm^{-1}) and for this reason luminescence can make a significant contribution to it.

In Refs. 31, 37, and 38 it was demonstrated for the example of NH_3 molecules that the obtained experimental results can be interpreted qualitatively and even quantitatively on the basis of the RV theory of RHRS proposed by the authors (see Sec. 1.6), and the study of the RHRS excitation spectra makes it possible to determine the possible channels for the scattering process and, moreover, to obtain information about the dephasing constants of the excited RV levels and to draw a conclusion based on it regarding the mechanism of dissociation of the molecules.

The RHRS spectra were excited by frequency-tunable pulsed radiation, obtained by mixing the radiation of a liquid-dye laser (pumped by the second harmonic of the YAG:Nd^{3+} laser) and its first harmonic (1064 nm). The power density of the pulses was equal to about 100 MW/cm^2 and the pulse repetition frequency was equal to 10 Hz. The scattered radiation was recorded in a 90° geometry. The spectral equipment was a simple monochromator with a resolution of 5–6 cm^{-1}. The spectrum was scanned once. The RHRS spectra were obtained when the doubled frequency of the incident light coincided with the vibronic absorption bands $v_2'' = 1$, 2, and 3 of the transition $^1A_1' - {}^1A_2''$ (the maxima of the 425.6, 417.8, and 409.8 nm bands,respectively[31]). The excitation spectra for a number of lines in RHRS were measured by scanning the doubled excitation frequency near and inside the bands $v_2'' = 2$ and 3 (419–416 and 411–407 nm, respectively[38]). To eliminate the absorption of the scattered light, the quantitative analysis of the spectra was performed near the combination tone $\nu_1 + \nu_2^a$, whose Stokes shift is equal to 4000 cm^{-1}. The pressure in the working cell was equal to 1–3 atm (the content of molecules was equal to about 0.1 M).

Figure 1 shows the scoping spectra of ammonium for two-photon (RHRS) and single-photon (RRS) excitations in the same absorption band $v_2'' = 2$. Before analyzing the spectra we shall describe the vibronic structure of the absorption for NH_3 molecules.

The absorption spectrum of ammonium in the region of the electronic transition under study contains a progression at the frequency ν_2 of the out-of-plane bending vibration of the molecule. The inversion in the molecular vibrations splits the v_2 level into a symmetric and asymmetric pair a_1' and a_2''. The corresponding scheme of vibronic levels as well as the transitions occurring in the RS and HRS processes is shown in Fig. 2.[37]

Since the splitting of the lower level is comparatively small and is equal to about 0.74 cm^{-1}, vibronic symmetry A_1' and A_2'' can be assigned with equal probability to the molecule in the ground state. In the D_{3h} symmetry group, to which the NH_3 molecule belongs, the single-photon transition A_1'–A_2'' is allowed in the dipole approximation, while the two-photon transition, on the other hand, is forbidden, and in addition only the vibronic (Herzberg–Teller) interaction between the electronic states via the asymmetric vibration $\nu_2(a_2'')$ can remove this forbiddance. In this case, as was shown in Part 1 of this review, the term B in the expression for the components of the quadratic-polarizability tensor makes the main contribution to the intensity of RHRS. Chung and Ziegler[37] analyzed all possible channels of RHRS for ammonium molecules, taking into account the fact that the vibrational transitions $a_1' \to a_1'$ and $a_2'' \to a_2''$ are allowed in

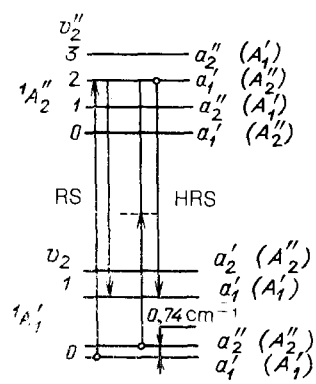


FIG. 2. Diagram of the energy levels of NH_3 along the coordinate v_2 for D_{3h} symmetry. The electronic, vibrational, and vibronic (in parentheses) symmetries of the levels as well as one of the possible channels of RRS and RHRS processes are indicated.[37]

RS and the transitions $a_1' \to a_2''$ and $a_2'' \to a_1'$ are allowed in HRS. It is obvious that in this case the lines of asymmetric vibrations ν_1^a and ν_2^a and their asymmetric overtones and combination tones of the type $(2n+1)\nu_i^a + m\nu_j^s$, where i, $j = 1, 2$ and $m = 0, 1, 2, \ldots$, and $n = 1, 2, \ldots$, should be observed in the RHRS spectrum, while lines corresponding to the symmetric vibrations ν_1^s (3461 cm^{-1}) and ν_2^s and their symmetric overtones and combination tones $n\nu_i^s + 2m\nu_j^a$, where $i, j = 1, 2$ and $m, n = 0, 1, 2, \ldots$, should be observed in the RRS spectrum. Since ν_2^s and ν_2^a differ by only ~ 0.74 cm^{-1} and ν_1^s and ν_1^a differ by an even smaller amount, the RRS and RHRS spectra in Fig. 1 are identical.

The RHRS spectrum of NH_3 molecules was analyzed theoretically in Refs. 31 and 38 based on the theory of rotational HRS,[28,30] developed in terms of the irreducible spherical tensor operators. It was shown there that the intensity of HRS by symmetric-top molecules is determined in the general case by five scattering invariants $|\beta^{l,Q}|^2$, which are given in Eq. (1.26) of this review. The expression for this tensor, corresponding to the conditions of the experiment performed in the work under discussion and taking into account the terms that are in resonance with the doubled excitation frequency, has the form of Eq. (1.27). In application to NH_3 molecules the latter expression corresponds to the term B. Because the two-photon transitions $^1A_1 \to {}^1A_2''$ are forbidden one of the matrix elements of the RV transitions $(M_p)_{gv}^{sv'}$ or $(M_p)_{sv'}^{ev'}$ in Eq. (1.27) will be formed by the vibronic interaction between the appropriate electronic states by means of the vibration $\nu_2^a(a_2'')$. This will result in a decrease of the integrated intensity of RHRS and the appearance of VR transitions, referring only to the vibration ν_2^a and its asymmetric overtone, in the spectra. At the same time, the relative intensity of the rotational components in the RHRS spectrum, which belong to the allowed vibrational transition and which are determined in Eq. (1.27) by the factors containing rotational quantum numbers, remains unchanged.

According to the J and K selection rules for RHRS in ammonium, five resonance RV levels with $J'' = J-2$, $J-1$, J, $J+1$, and $J+2$ are possible. This results in the appearance of lines from seven rotational branches — N, O, P, Q, R, S, and T. Analysis also showed that the intensity of the RHRS line belonging to a definite branch is determined by one or several channels of the process proceeding through different resonance RV states, for which some component of the tensor $|\beta^{l,Q}|^2$ or several components together are responsible. By comparing the experimental spectra it is possible to determine the contribution of separate components $|\beta^{l,Q}|^2$ to the intensity of RHRS.

Figure 3 shows a section of the RHRS spectra of the NH_3 molecules studied in the region of the $\nu_1 + \nu_2^a$ vibration, where the structure owing to the rotational transitions is resolved.[31] It was found that lines corresponding only to the P, Q, and R branches appear in the spectrum; this is indicated in the figure. This is possible in the case when the component of the scattering tensor $|\beta^{1,0}|^2$ makes the main contribution to the intensity. Estimates showed that the contribution of components with Q = 2 is equal to about 5%. An analogous picture was also observed in the case of resonance excitation with the absorption bands $v_{2=1}''$ and $v_2'' = 3$.

In this situation the expression (1.27) for the intensity

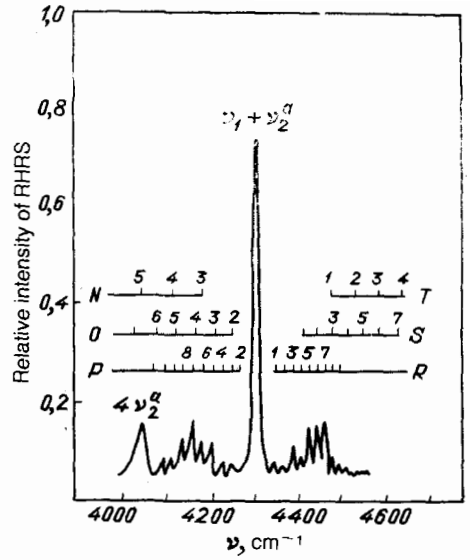


FIG. 3. The section of the RHRS spectrum of NH_3 in the region of the vibration $\nu_1 + \nu_2^a$. The resonance with the band $v_2'' = 2$. It is shown how the bands corresponding to different branches should be arranged.[31]

of RHRS in transitions with $J'' = J-1, J, J+1$ (P, Q, and R branches) in the laboratory coordinate system assumes the form

$$I \sim |\beta^{1,0}|^2 = \frac{J^2 - K^2}{J} G_Q^0 \text{ — P-branch,}$$
$$= \frac{K^2(2J+1)}{J(J+1)} G_Q^0 \text{ — Q-branch,}$$
$$= \frac{(J+1)^2 - K^2}{J+1} G_Q^0 \text{ — R-branch,} \qquad (2.1)$$

where

$$G_Q^0 = \left| \sum_{s,v'} \frac{(M_z)_{ev''}^{gv''} [(M_x)_{sv'}^{ev''} (M_x)_{gv}^{sv'} + (M_y)_{sv'}^{ev''} (M_x)_{gv}^{sv'} + (M_z)_{sv'}^{ev''} (M_z)_{gv}^{sv'}]}{(\omega_{gv,sv'} - \omega)(\Delta_Q - i\Gamma_{ev''}^{J''K''}/2)} \right|^2,$$

and

$$\Delta_Q = \omega_{gv,ev''} + (B_{v''} - B_v) J(J+1) + [(C_{v''} - B_{v''}) - (C_v - B_v)] K^2 - 2\omega$$

is the detuning of the doubled frequency of the exciting radiation from the frequency of the resonance RV transition of the Q branch with fixed J; B and C are the rotational constants of a symmetric top. It can also be seen from the expressions presented above that the excitation spectra of the RHRS lines in the case of the P, Q, and R branches have one resonance of the Lorentz type whose width is determined by $\Gamma_{ev''}^{J''K''}$, which, generally speaking, depends on J''.

Indeed, the experimentally obtained excitation spectra for the RHRS lines of rotational transitions in the R branch in resonance with the bands $v_2'' = 2$ and $v_2'' = 3$ (Ref. 38) confirm the existence of a single resonance, approximated well by a contour of the Lorentz type with one adjustable parameter $\Gamma_{ev''}^{J''K''}$; this is illustrated in Fig. 4. A fit of this type was employed in Ref. 38 in order to measure the width of the resonances of the RV levels of NH_3 for $v_2'' = 2,3$ and $J'' = 1-8$ and to determine the corresponding total-dephasing times. The values obtained agree well with the times found previously for $v_2'' = 2$ by the RRS method, and they

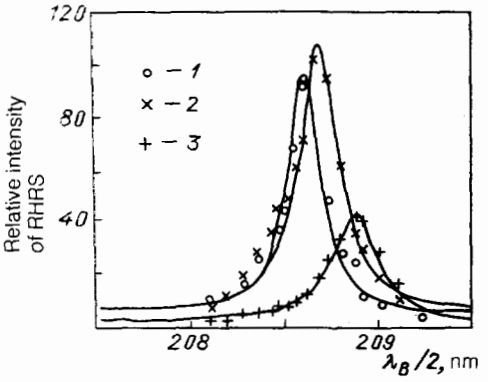


FIG. 4. The experimental excitation spectra of the lines of RHRS by NH_3 belonging to the R-branch with $J'' = 2$ (*1*), 4 (*2*), and 7 (*3*). The result of the approximation using the formula (2.1) with $\Gamma = 47, 59$, and 64 cm^{-1} for $J'' = 2$, 4, and 7, respectively, is shown.[38]

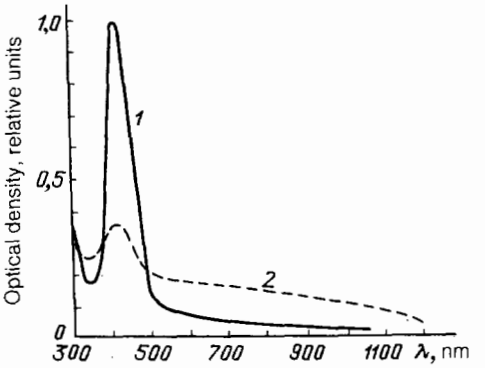


FIG. 5. The extinction spectra for the starting (1) and aggregated (2) silver hydrosols.[40]

exhibit an analogous dependence on J'': they decrease from 119 to 76 fs as J'' increases from 1 to 8. This fact as well as the agreement between the relative intensities and the computed value obtained from formula (2.1) confirm that the proposed theory describes the RHRS process correctly. A similar dependence was observed for $v_2'' = 3$–as J'' increased from 1 to 8 the total-dephasing times ($\tau = 2\pi c/\Gamma_{ev''}^{J''K''}$) decreased from 68 to 47 fs.

Since the constant $\Gamma_{ev''}^{J''K''}$ is determined by photodissociation, and in particular by the process $NH_3 \rightarrow NH_2 + H$, it was found that it is possible to investigate the effect of rotational motion on this process. The fact that the photodissociation constants depend on the quantum number J'' for $v_2'' = 2$ and 3 enabled Chung and Ziegler[38] to conclude that the centrifugal mechanism for the lowering of the barrier to tunneling of the H atom is the dominant mechanism in the process of photodissociation of NH_3 molecules when they are excited into the $v_2'' = 2$ levels of the $^1A_2''$ state.

Although analogous information can also be extracted from the RRS spectra[39] the RHRS method is preferable in this case. Since for NH_3 molecules one of the invariants of the scattering tensor makes the main contribution to RHRS, the spectrum contains only three rotational branches, whose excitation spectra have one resonance. This makes it much easier to analyze these spectra than the RRS spectra, where three types of resonances lead to the appearance of five branches with overlapping lines. In addition, two-photon excitation with restructuring of the frequency in the far-UV region is much easier to achieve than single-photon excitation because of the greater availability of excitation sources.

We note that because under the conditions of two-photon resonance the absorption losses of the radiation exciting RHRS in the medium under study are vanishingly small a much larger, than in the case of RRS, number of scattering centers can be included in the scattering process by increasing both the illuminated volume and the concentration of centers. In the papers cited above this made it possible to obtain RHRS signals for NH_3 that were comparable in absolute magnitude to the RRS signals.[35]

2.2. Organic-dye molecules

In this section we shall present the results for RHRS by organic-dye molecules. These results were obtained with adsorption of the molecules on aggregated particles of colloidal silver, i.e., under conditions of surface-enhanced amplification of the signals recorded.[40–48] This made possible a sharp (by up to a factor of $\sim 10^4$) enhancement of the spectra; this was first shown experimentally in Ref. 40. At the same time, the adsorption brought about a radical suppression of the luminescence background, and this made it possible to obtain RHRS spectra of luminescing dyes as well as their RRS spectra, necessary for making comparisons. The starting sol was prepared by using hydrogen to reduce Ag_2O in water[49] and contained spherical particles with an average diameter of ~ 30 nm. Aggregation was achieved by adding $2 \cdot 10^{-2}$ M of NaCl solution, as a result of which compact clusters with an average size of 150–200 nm formed. The extinction spectra of the starting and aggregated hydrosol are presented in Fig. 5.[40]

The enhancement produced in the standard RS when molecules are adsorbed on the rough surface of different metals, in particular, silver, has been studied in detail and comprehensively in the last 15 years.[50,51] Most results obtained in these studies are also valid for nonlinear processes. We shall summarize the main results of relevance here.

It is generally recognized that surface enhancement is caused by chemical or electromagnetic mechanisms acting separately or simultaneously.[51] The first mechanism is specific to the type of adsorbate molecule and is connected with the formation of chemical complexes, for example, charge transfer with the absorption band falling into the region of excitation of the spectra. As a result of this their intensity increases in a resonance fashion. In the process, as a rule, appreciable restructuring of not only the electronic but also the vibrational system of energy levels is observed. This is manifested as a change in the position, number, and relative intensity of the spectral lines of adsorbed molecules and is also reflected in their excitation spectra. The second mechanism is connected with the local intensification of the effective electric field, acting on a molecule near the surface of the metal when local plasma oscillations (local plasmons, LPs) are excited in them and does not depend on the type and, in general, the presence of adsorbed molecules on the surface. It is this mechanism that is responsible for the sharp enhancement of the efficiency of second-harmonic generation by a rough surface or by a system of ultradispersed particles of metal.

To resolve the question as to how useful are the data on vibrational and vibronic spectroscopy of molecules in solutions for analyzing the RHRS spectra of adsorbed mole-

cules, the RRS spectra, obtained under comparable excitation conditions, of admolecules and molecules in solutions were compared. In those cases when such a comparison could be made it was found that the spectra are virtually identical with respect to the set and relative intensity of the lines.[44,45] In other cases,the comparison was made using the RRS spectra of solid solutions of dyes in KBr; this procedure is less accurate.[46,47]

For the vibronic spectra it was possible to compare the absorption spectra or the RRS excitation spectra, which carry analogous information, of molecules in solutions with the RRS excitation spectra of admolecules. It was found that their positions and widths agree well with one another.[52]

The results obtained indicate that adsorption has a comparatively weak effect on the vibrational electronic subsystems of the molecules and they give a basis for using the data, required for analysis, for molecules in solutions (the position and width of the vibronic transitions and the cross sections for single- and two-photon absorption).

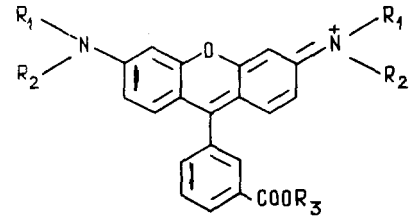
In Refs. 40 and 41 it was found that the increase in the intensity of RHRS by adsorbed molecules is observed simultaneously with the appearance of an absorption band of the hydrosol, accompanying aggregation of its particles, near the wavelength of the exciting radiation (1064 nm). According to Ref. 53 this band is associated with the excitation band of the local plasmons. A sharp increase in the scattering into the second harmonic (SSH) was also observed at the same time. This behavior is characteristic for the electromagnetic mechanism, where the HRS and SSH enhancement factor has the form[51] $K(\omega_p) \sim |g(\omega_1)|^4 |g(\omega_p)|^2$ (the factors $g(\omega_i)$ and $g(\omega_s)$ describe the intensification of the local field at the frequency of the exciting (ω_i) and scattered (ω_s) radiations). This, combined with the fact, noted above, that adsorption does not strongly affect the vibronic spectra of the molecules, made it possible to conclude that the electromagnetic mechanism makes the dominant contribution to the enhancement of RHRS by dye molecules, studied in Refs. 40–48. The predominance of the electromagnetic mechanism, together with the fact that in the systems studied the intensity of SSH is determined primarily by scattering by silver particles,[46] gave a basis for using the SSH signals as an internal reference for studying the contributions of molecular resonances to the intensity of RHRS.[47]

The sharp increase in the efficiency of the RHRS process accompanying adsorption of molecules, together with the effect of molecular resonances, made it possible to record with the help of the standard apparatus intense and informative RHRS spectra from many rhodamines, pyronins, and other dyes belonging to the class of acridine, indigoid, polymethine, etc., dyes, which have long-wavelength single-photon absorption bands at wavelengths in the range 500–1000 nm.

The RHRS spectra were excited with 1064 nm radiation from a quasi-cw YAG:Nd^{3+} laser with a peak power of 10 kW and pulse repetition frequency ~ 10 kHz. The second-harmonic radiation of the same laser or of an ion argon laser was used to obtain the enhanced and standard RRS spectra. The spectral instrument consisted of a DFS-24 double monochromator with d.c. amplification. In comparing the RHRS and RRS spectra it was assumed that the lines being compared refer to different types of vibrations, if the difference in their frequency was not less than 4 cm^{-1}. Dyes which are insoluble in water were introduced into the silver hydrosol through intermediate solvents—acetone, ethanol, and pyridine. The typical molecular concentrations in the volume were equal to 10^{-6} M, and in some cases they were two orders of magnitude lower.

Since it was shown earlier that the two-photon absorption bands play the same role in the RHRS process as do single-photon absorption bands for RRS, we shall first discuss the compounds whose TPA spectra are known or for which the available information on TPA is less detailed. These include the rhodamines 6G and 110 (P6G and P110, respectively) as well as acridine orange (AO). In Ref. 54, the TPA spectra of the first two dyes were obtained in Ref. 54, and the TPA cross sections were measured for AO while in Ref. 55 the symmetry of the lower electronic states was determined.

We also note that the choice of the objects of study named above on the whole permits making a more systematic comparison of the experimental and theoretical results. The rhodamine and the related xanthene dyes have a structural formula of the following form



where $R_{1,2}$ = H, CH_3, C_2H_5 and R_3 = H, C_2H_5. Pyronins and acridine red do not have a phenyl radical, and in the xanthene fragment in AO the heteroatom O is replaced with N.

Aristov *et al.*[56] established that the presence of a carboxyphenyl group in rhodamines does not significantly affect the π-electron structure of the xanthene fragment (which determines the properties of the lower electronic levels of the molecules) because the planes of both fragments are orthogonal to one another. Because of this, the symmetry of the electronic levels of the molecules is on the whole the same as that of the xanthene chromophore (C_{2v}).

According to the theoretical calculations of Ref. 56 and the polarization measurements of the SPA and TPA spectra of rhodamines[55–58] as well as their luminescence spectra, the scheme of the corresponding electronic levels has the form shown in Fig. 6. The dipole moment of the single-photon transition $S_0 \to S_1(1^1A_1 - 1^1B_2)$ lies in the x, y plane of the xanthene frame and is oriented along the long y axis. The dipole moments of the transitions $S_0 \to S_n$, where $n = 2$, 3, and 4 is approximately an order of magnitude smaller, and in addition in the case $S_0 \to S_2$, $S_0 \to S_4(A_1 \to A_1)$ they are oriented along the z axis. The SPA spectrum of the P6G molecules is presented in Fig. 6. Although in the C_{2v} group the single- and two-photon transitions between the states A_1 and B_2 are formally allowed simultaneously, the experimental data for TPA in P6G (Ref. 54; curve *3* in Fig. 6) show that the transition $1^1A_1 \to 1^1B_2$ is in reality very weak and is allowed primarily by the nontotally symmetric vibrations b_2 owing to the vibronic interaction between the states $S_1(B_2)$ and $S_4(A_1)$, since the two-photon transition into the S_4 state, according to Ref. 57, is strongly allowed for R6G molecules and is characterized by a cross section that is two orders of

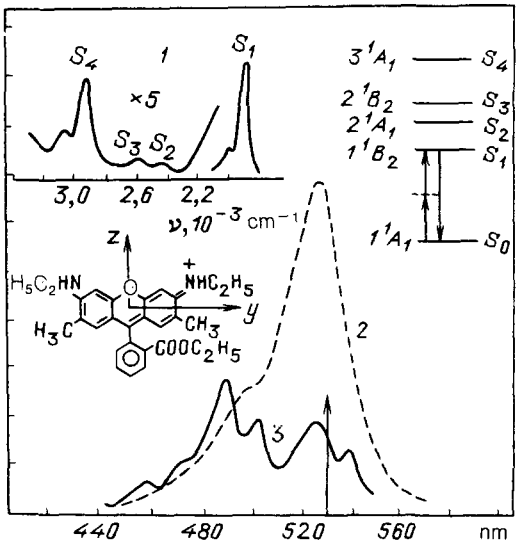


FIG. 6. 1) The SPA spectrum of rhodamine 6G in ethanol at 77 K;[58] 2) and 3) the SPA and TPA spectra, respectively, of the dye at 300 K.[54] The structural formula and the scheme of the electronic levels with an indication of their symmetry are presented. The position of the doubled frequency of the exciting light is shown.

magnitude larger. The situation is similar in the case of R110.

The RHRS and RRS spectra for R6G molecules in the fundamental region are presented in Fig. 7. It is obvious that both types of spectra differ from one another with respect to both the frequencies of almost all lines and the distribution of the intensities. The negligibly low intensity of the lines in the "low-frequency" (<1190 cm^{-1}) region of the RHRS spectrum is interesting. Analogous features were also observed in the case of the rhodamines 3B, 1/2B, and 110. We note that the RHRS spectra of the last two dyes are, respectively, ~ 10 and 100 times weaker than the spectra of R6G; this is comparable to the decrease in the sharpness of the resonance.

The characteristics established can be qualitatively explained on the basis of the theory of RHRS presented in Part 1 of this review.[45] Indeed, resonance with a strong SPA band results in the enhancement predominantly of the fully symmetric vibrations (a_1) in the RRS spectra of the R6G molecules (see Fig. 7b) and is determined by the Franck–Condon term A.[6,7] However the RHRS spectrum of R6G molecules is excited in the region of the weak TPA band, which is allowed because of the Herzberg–Teller interaction. The term B (formula (1.10)) now makes the main contribution to the intensity of RHRS; this is the reason for the selective enhancement of those nontotally symmetric vibrations that most actively mix the S_1 and S_4 states. In the case when the symmetry of the xanthene frame (C_{2v}) is preserved when the molecules are excited into the states S_1 and S_4, the vibrations that mix must have b_2 symmetry, since the transition moments of the transitions $S_0 \to S_1$ and $S_0 \to S_4$ are directed along the y and z axes, respectively, and $B_2(y) \times b_2 = A_1(z)$. Thus the nontotally symmetric vibrations b_2 are manifested in the RHRS spectrum of the R6G molecules; this is why the RHRS spectrum is clearly distinguished from the RRS spectrum. An analogous conclusion can also be drawn for the other dyes mentioned above (rhodamines 3B, 1/2B, and 110).

A comparative analysis of the RHRS and second-order RRS for the rhodamines 6G and 3B also leads to the same results. Figure 8 shows as an example the RHRS spectrum of rhodamine 6G in the regions of the fundamental and first overtone.[43] One consequence of the vibronic theory of

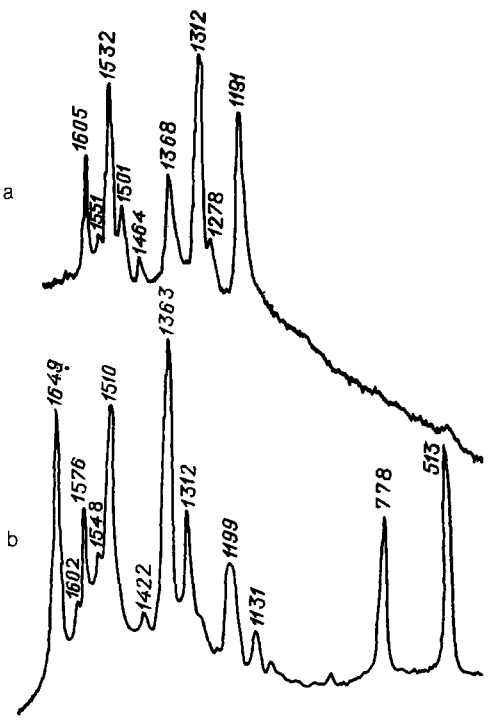


FIG. 7. The RHRS (a) and RRS (b) spectra of rhodamine 6G adsorbed on particles of silver. The frequencies of the lines are shown in cm^{-1}.

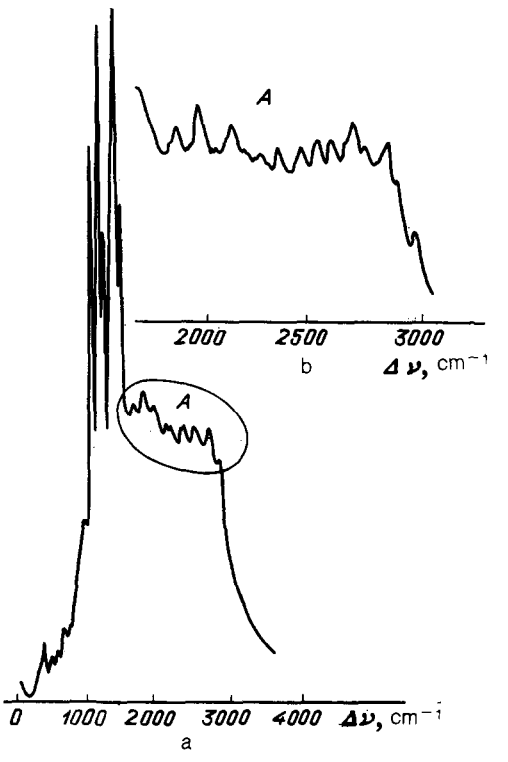


FIG. 8. The RHRS spectrum of rhodamine 6G (a) and its overtone region in greater detail (b).[43] The frequencies of the overtone vibrations and their interpretation are presented in Table I.

TABLE I. Identification of the overtone bands in the RHRS spectrum of rhodamine 6G (Ref. 43).

Frequencies of the spectral lines, cm^{-1}			Frequencies of the spectral lines, cm^{-1}		
RHRS overtones	RHRS lines	RRS lines	RHRS overtones	RHRS lines	RRS lines
1805	1191	613	2695	1191	1510
1917	1312	613	2733	1532	1199
2100	1312	778		1368	1363
2387	1191	1199	2835	1191	1649
2495	1191	1312	2891	1532	1363
2564	1368	1199	2959	1312	1649
2629	1312	1312	3177	1532	1649
				1605	1576

RHRS is that in the case when the term B predominates the overtone region will also contain lines of the nontotally symmetric vibrations, which, in our case, also have b_2 symmetry. On the other hand, the symmetry of the overtones and the combination tones is determined by the symmetry of the initial fundamental vibrations. Since the C_{2v} symmetry group allows for one possibility of formation of higher order tones of lower symmetry ($b_2 = b_2 \times a_1$), it should be expected that only one of the combination tones, formed by two vibrations, one (a_1) active in RRS and the other (b_2) active in RHRS, should appear in the region of the first overtone of the RHRS spectrum. This result is completely confirmed experimentally (Table I).[43] This makes it possible to explain the existence of a common line (~ 1312 cm^{-1}) in both spectra as a random coincidence of the frequencies of vibrations with different symmetry. The results obtained for the rhodamines studied also allow us to conclude that in this case the relative intensity of the RHRS lines in the fundamental and overtone regions corresponds to the estimates made on the basis of the proposed theory of the process.

One of the dyes belonging to the acridine class—acridine orange (AO), whose RHRS and RRS spectra contain the same collection of lines with close relative intensities—exhibits a qualitatively different behavior. This can be seen in Fig. 9. As we have already pointed out, the structure of the AO molecules is analogous to that of the pyronin (P) molecules, but the heteroatom is N rather than O. This substitution, however, does not change the symmetry and therefore the electronic states of the chromophore. The significant difference between AO and the rhodamine dyes lies in the fact that in AO the cross section of TPA for the transition $S_1 \rightarrow S_0$, which was measured directly in Ref. 55, is characteristically very large. This fact, as well as comparison of the cross sections of TPA of linearly and circularly polarized light, gave a basis for Foucaut and Hermann[55] to conjecture that the S_0 and S_1 states in this case have the same symmetry. At the same time direct measurements show that this transition is also intense in SPA (see inset in Fig. 9). The possible matching of these results is made in Ref. 55 based on the quantum-chemical analysis and taking into account the specific nature of the contribution of different electronic configurations in the S_1 state of acridines.[59] From the standpoint of the vibronic theory of RHRS it is significant that in this situation for both types of spectra—RHRS and RRS—the same electronic state (S_1) into which one- and two-photon transitions are strongly allowed is the resonance state. Then the intensity of both scattering processes is determined by the Franck-Condon mechanism (the term A), with which the predominant enhancement of the totally symmetric vibrations (A_1) in the spectra of each type and therefore the identity of the latter is associated; this is in fact what is observed experimentally.

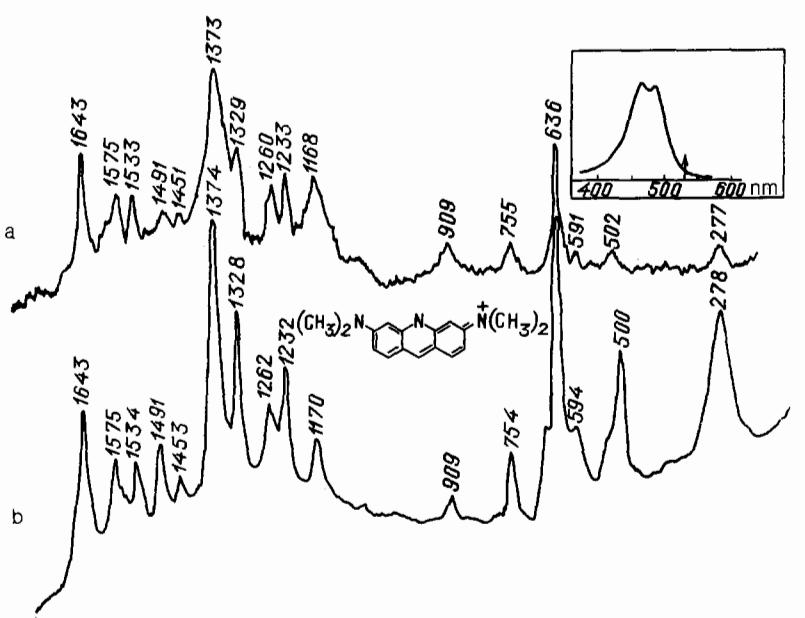


FIG. 9. The RHRS (a) and RRS (b) spectra of acridine orange.[45] The structural formula and the position of the long-wavelength SPA band of the dye are presented.

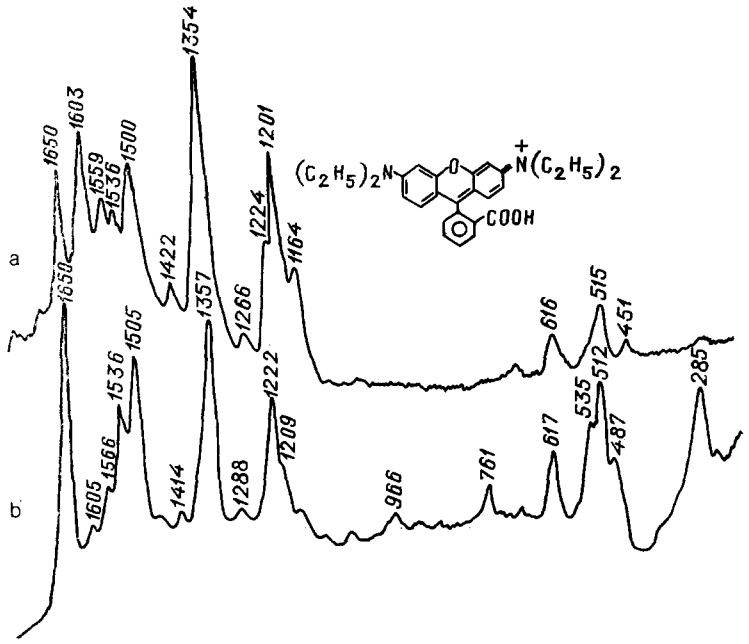


FIG. 10. The RHRS (a) and RRS (b) spectra of rhodamine S.[45]

We also note that according to the measurements performed in Ref. 45 the intensities in the RHRS spectra of the R6G and AO molecules are comparable. At the same time the theory predicts that the contribution of the term A to the intensity of the scattering is approximately two orders of magnitude larger than that of the term B. But this is valid only in the case when the transition moments are equal and when the resonance conditions of excitation are the same. Taking into account the fact that for AO the resonance is less sharp and the transition moments are smaller than for the R6G molecules shows that there is no disagreement with the theory.

Interesting results, though less convincingly interpretable, have also been obtained for a number of other rhodamines and dyes of close classes. In Ref. 45 it was established that in the RHRS and RRS spectra of the rhodamines B and C, in which the frequencies of the lines generally do not correspond to one another, lines in the comparatively low-frequency region (frequencies less than ~ 1150 cm^{-1}) are intensified, and, in addition, in these spectra of rhodamine S, pyronins B and Zh, and acridine red, there appear many common lines, including also the ~ 1650 cm^{-1} line, which apparently belongs to the totally symmetric vibrations of the C=C bonds of the xanthene frame; this is illustrated for rhodamine S in Fig. 10.

As regards the intensification of the comparatively low-frequency vibrations, if the term B makes the dominant contribution to the scattering, this could indicate, for example, that the plane of the xanthene frame of these molecules is deformed in a manner comparable to the lowering of the symmetry of the molecule to C_2. In this case the out-of-plane deformation vibrations with symmetry b_1 can participate in the mixing of the electronic states and can be manifested in the RHRS. It is natural to attribute the weaker rigidity of the xanthene frame in this group of molecules to the fact that such molecules do not have a carboxyphenyl group, which, according to Ref. 60, lowers the mobility of the amino group in the excited state.

On the other hand, the observation of totally symmetric vibrations, whose intensity is comparable to that of the nontotally symmetric vibrations, in the RHRS spectra indicates that the relative contribution of the term A, which, generally speaking, is not symmetry-forbidden for this group of molecules, to RHRS increases. Adequate changes should also be observed in the TPA spectra of the same molecules. Unfortunately, there are no such data in the literature, and this makes it impossible to draw the correct conclusions about the details of the RHRS process in this case, when it is simultaneously determined by the Franck–Condon and Herzberg–Teller mechanisms. Information that can usually be extracted by comparing the excitation spectra of RHRS and the TPA spectra could also be useful.

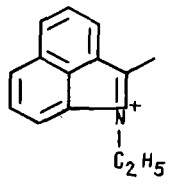
There are situations, however, when the combined study of even three types of vibrational spectra—RRS, RHRS, and IR absorption—still does not give unambiguous proof of the true structure of the molecules. An example is the dye of the triphenyl methane class, the so-called crystalline violet.[44,45] The reason probably lies in the fact that the absence of analytical spectral lines of RRS or RHRS could be connected not only with the violation of the selection rules but also with the low intensity of the lines, in particular, owing to the different sharpness of the resonances.

A fundamental feature of RHRS, as compared with RRS, as we have already mentioned, is that double resonances (DRs), when the conditions for the fundamental (ω_1) and doubled ($2\omega_1$) frequencies of the exciting light to be close to the real energy states of the scattering centers (the expression (1.3)) are satisfied, can in principle occur. Idealized estimates show that in this case the efficiency of the process can be higher than the single-resonance process by another factor of 10^3–10^6.

To study in detail double resonances in molecular systems with nonuniformly spaced electronic levels it is apparently necessary to excite RHRS with radiation at two different frequencies, one of which (or both) can be varied. Nevertheless Baranov *et al.*[47] were able to follow experimentally the effect of double resonances on the efficiency of the "degenerate," i.e., with excitation at one frequency, RHRS

by molecules of polymethine dyes, characterized by systems of electronic levels with the same symmetry but different energy parameters.

The integrated intensities were compared of RHRS by molecules of pseudoisocyanine (PIC) and a number of molecules of the polymethine class with the structural formula $R^+—CH=(CH—CH)_n=R$, where R^+ is



and $n = 1$, 2, and 3, which have C_{2v} symmetry and are arbitrarily denoted by the numbers 1, 2, and 3, respectively.

The SPA spectra obtained and the scheme of electronic levels of the molecules are shown in Fig. 11. The exchange interaction leads to splitting of the $2A_1$ state into three levels (denoted in the diagram by the symbols (+), (°), and (−)) and to the appearance of an additional (though weak) selection rule for a transition between states of different parity.[61] In particular, the single- and two-photon transitions are strongly allowed simultaneously between the states $1A_1^- \to 1B_2^+$ and $1A_1^- \to 2A_1^\circ$, and it is precisely these two channels that should be expected to make the greatest contribution to the intensity of RHRS. In the SPA spectra, to these transitions correspond the S_1 and S_3 bands (for PIC the band corresponding to S_3 is not shown; it has a maximum near ~320 nm).

To the usual conditions under which the enhanced RHRS spectra are obtained and which were enumerated above we add the fact that in order to eliminate the thermal defocusing of the exciting radiation the silver sol in this case was prepared based on heavy water, and the dyes themselves were introduced into it through their solutions in pyridine. The integrated intensity of the scattered radiation was normalized with respect to the second harmonic, taking into account both the losses of the exciting and shifted radiations and the effect of the local field near the particles of silver. We also note that as the fundamental frequency (ω_i) approaches the long-wavelength band of SPA photodesorption of dye molecules from the silver, proportional to the average intensity of the IR radiation, was observed. This effect was eliminated by decreasing the energy of the pulses, and the proportionality of the intensity of RHRS to the squared intensity of excitation was used to monitor the absence of the effect.

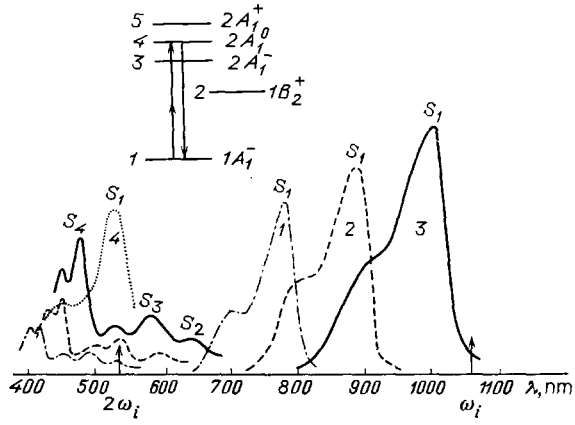


FIG. 11. The SPA spectra of the dyes *1–3)*, in pyridine; *4)* the analogous spectrum of PIC; the short-wavelength part of the spectra is magnified by a factor of 5. The positions of the fundamental and doubled frequencies of the exciting light are indicated. The scheme of the electronic levels of the dyes with an indication of their symmetry and the RHRS channel are indicated in the inset at the top. (From Ref. 47.)

The results of the measurements, refer to the intensity of RHRS by PIC molecules, for which a quite sharp resonance at $2\omega_i$ was realized, are presented in Table II.

According to the vibronic theory of RHRS in the situation when single- and two-photon transitions are allowed simultaneously, the term A plays the predominant role. This is also confirmed by the similarity of the RRS and RHRS spectra, observed in this case. Then

$$I_{\text{RHRS}} \sim K\{[(\omega_{41}-2\omega_i)^2+\Gamma_{41}^2]^{-1}[(\omega_{21}-\omega_i)^2+\Gamma_{21}^2]^{-1} + [(\omega_{21}-2\omega_i)^2+\Gamma_{21}^2]^{-1}[(\omega_{41}-\omega_i)^2+\Gamma_{41}^2]^{-1}\}, \quad (2.2)$$

where $K \sim |M_{12}M_{24}M_{41}|^2 I_0^2$, ω_i and I_0 are the frequency and intensity of the exciting radiation, ω_{ij} is the frequency of the electronic transition $i \to j$, Γ_{ij} is the total width of the transition $i \to j$, and $|M_{ij}|^2 = |M_{ji}|^2$ is the dipole moment of the transition $i \to j$. The expression (2.2) reduces to the expressions (1) and (2) from Ref. 47 for the intensity of RHRS by PIC molecules and molecules of the dyes 1, 2, and 3.

The experimentally obtained values of the intensity of RHRS indicate that the resonances at ω_i and $2\omega_i$ operate simultaneously. The comparatively small increase in the intensity of RHRS owing to the resonance at ω_i is connected with the fact that while resonance conditions at ω_i are improved the conditions at $2\omega_i$ are degraded. Estimates of the intensity of RHRS are presented in Ref. 47. These estimates were made under the assumption that the level $2A_1^+$, into

TABLE II. The relative intensities of RHRS by molecules of polymethine dyes. The experimental data and the results of estimates based on the formulas (2.2). The parameters of the transitions were obtained from the SPA spectra (see Fig. 11).

Dyes	Relative intensity of RHRS		Parameters of the transitions employed for the estimates			
	Experiment	Estimate	ω_{31}, cm^{-1}	ω_{41}, cm^{-1}	Γ_{31}, cm^{-1}	Γ_{41}, cm^{-1}
PIC	1	1	18 870	31 250	590	600
1	2,1	2,0	12 930	20 745	360	600
2	55	58	11 390	18 800	335	600
3	67	73	10 030	17 310	355	600
$\omega_{21} = \varphi_i$ $\omega_{31} = 2\omega_i$	—	2400	9 397	18 794	350	600

which the intense transition $1A_1^- \to 2A_1^+$ is allowed (the S_4 band in the SPA spectrum), is the intermediate state (r). However important features of the experimental data contradict this assumption.

Although the computed value of the enhancement factor, presented in Table II, for exact resonances at ω_i and $2\omega_i$ and for the typical parameters of the transitions in the molecules studied is quite high (~ 2000) it cannot be realized in the variant of "degenerate" RHRS. Nonetheless even in this case the increase obtained in the intensity of RHRS by optimizing the resonance conditions is about two orders of magnitude. This suggests that it may be possible to record RHRS spectra of molecules in the standard solutions with the help of the traditional technique employed in Raman-scattering studies.

We shall conclude this section of the review with a brief discussion of the results of the study of RHRS spectra of a group of indigoid dyes.[46] The distinguishing feature of the molecules of these dyes is that they are photochromic and exist in the form of stable cis- and trans-isomers with C_{2v} and C_{2h} symmetry, respectively. In Ref. 62 it is shown that adsorption does not prevent photoisomerization, though it does change the rate of photoisomerization. It is advantageous to perform the excitation with radiation with wavelength $\lambda = 1064$ nm, since radiation at this wavelength does not give rise to phototransformations, which can be controlled by additional irradiation in the SPA band in the visible region of the spectrum; this technique was employed in Ref. 46.

It was found that the RHRS spectra obtained belong exclusively to cisisomers of the dyes, since according to the estimates the intensity of the RHRS lines of the transisomers is lower by at least a factor of 10^2. This corresponds to the expected results for centrosymmetric molecules.

A comparative analysis of the RRS and RHRS spectra of one of the dyes studied—perinaphthothioindigo (PNTI)—gave a basis for suggesting that the strongest lines in the RHRS spectrum refer to vibrations with b_2 symmetry; this is consistent with the fact that the B term makes the main contribution to RHRS, while nontotally symmetric vibrations are also manifested in the RRS spectra of the same molecules in addition to the totally symmetric vibrations, though, it is true, in the form of weaker lines. Shpol'skiĭ's spectra of thioindigo exhibit analogous behavior.[63] This behavior could be caused by the fact that two close absorption bands, between which there exists a vibronic interaction, are present in the region of the long-wavelength SPA of the transisomer of PNTI.

Baranov *et al.*[46] were also able to estimate correctly for PNTI the contribution of the adsorbed dyes to the enhancement of the second harmonic of the sol + dye system. The intensity of scattering into the second harmonic (SSH) was measured in parallel with the intensity of RHRS for PNTI as a function of the additional irradiation. It was found that when the efficiency of RHRS changed by an order of magnitude the SSH signal remained virtually constant. From here it may be concluded that the increase in SSH in the colloidal silver solutions employed is caused primarily by the silver particles themselves.

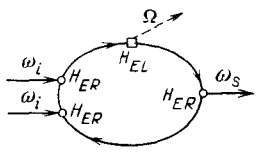


FIG. 12. Diagram of the HRS process in fourth-order perturbation theory. H_{ER} and H_{EL} are the electron-photon and electron-phonon interactions, ω_i and ω_s are the frequencies of the exciting and scattered light, and Ω is the phonon frequency. The contribution of the electron is illustrated.

2.3. Solid crystalline bodies

In order to understand better the experimental data presented below we shall make some general remarks about the process of HRS in solids. The process can be represented as a sequence of four electronic transitions (Fig. 12), induced by the electron-photon (H_{ER}) and electron-phonon (H_{EL}) interactions: a) electron-hole (e–h) pairs are created as a result of the interaction of an excitation photon (ω_i) with the crystal; b) under the action of the second photon (which, for simplicity, has the same frequency ω_i) the e–h pair passes into a new electronic state; c) the interaction of the electron (or hole) with the crystal lattice results in the formation of a photon (Ω) and the transfer of the e–h pair into a new electronic state; and, d) annihilation of the e–h pair gives rise to the emission of the scattered photon (ω_s) and the system returns into the initial electronic state. The possible diagrams for the three-band scheme of HRS in the case of intra- and interband H_{EL} for electrons and holes are constructed in Figs. 13a–d. The correspondence of the real energy bands to these schemes must be studied separately in each specific case. Thus for centrosymmetric media, when the phonons and the electronic states at the singular points of the Brillouin zone have a definite parity, the HRS process is allowed in the dipole approximation only if H_{EL} couples different bands.

In the literature there are no detailed calculations of the components of the tensor of HRS by phonons under resonance conditions of excitation of the spectra. Resonance effects in HRS of crystals can be understood qualitatively by using the expression for the components of the HRS tensor,[64] retaining only the resonance terms, corresponding to

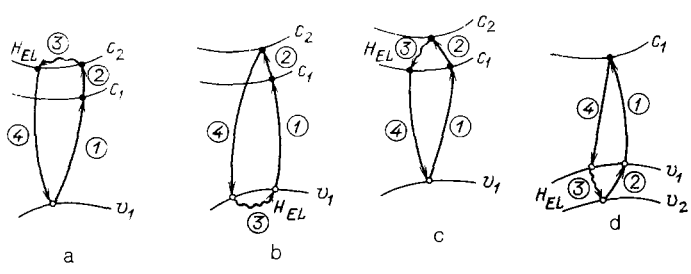


FIG. 13. The diagrams of the three-band scheme of HRS for the electronic (a, c) and hole (b, d) contributions in the case of intraband (a, b) and interband (c, d) H_{EL}. The transition sequences are indicated. v_i and c_i are, respectively, the valence bands and the conduction bands.

the diagrams in Fig. 13, and taking into account phenomenologically the finite width of the intermediate states. In this case the component of the HRS tensor has the form

$$\beta_{ijk} = C \sum_{\alpha,\beta,\gamma} \frac{d^i_{0\gamma} M_{\gamma\beta} d^j_{\beta\alpha} d^k_{\alpha 0}}{(E^\gamma - \hbar\omega_i - i\Gamma_\gamma)(E^\beta - 2\hbar\omega_i - i\Gamma_\beta)(E^\alpha - \hbar\omega_s - i\Gamma_\alpha)}, \quad (2.3)$$

where the indices i and j refer to the incident light, the index k refers to the scattered light, the index 0 refers to the initial state, the indices α, β, and γ refer to the intermediate states, d^i_{mn} are the matrix elements of the dipole moment of the transition $m \to n$, associated with H_{ER}, M_{mn} is the matrix element of the electron-phonon interaction in the transition $m \to n$, C is a constant, and $\hbar\omega_s = 2h\omega_i - \hbar\Omega$.

The expression (2.3) is structurally identical to the term B in the expression (1.7) for the component of the RHRS tensor for molecules. The additional factor in the denominator describes the so-called "output" resonance, when the frequency of the scattered light (ω_s) is close to the frequency of the electronic transition, and is analogous to the factor in the expression for the cross section for RRS derived in the static approximation.[65] Just as in RRS, the specific form of β_{ijk} is determined by the properties of the intermediate states—discrete (excitons, levels due to size quantization) or continuous—which arise, for example, due to the weakly coupled e–h pairs, and the type of electron-phonon interaction.[66]

Since the first observations of resonance effects in RHRS were made in Refs. 14, 67, and 68 and later extended in Ref. 69 in an investigation of a single crystal of CdS, we shall start our review of the results precisely with this semiconductor material, which has the same structure as wurtzite with the space symmetry C^4_{6v}. The RHRS spectra were obtained at an angle of 90° to the incident beam for different scattering geometries. The pulsed radiation with $\lambda = 1064$ nm from a YAG:Nd$^+$3 laser (the pulse $P = 30$–500 kW and the pulse repetition frequency was equal to 50 Hz) was used to excite the spectra. The spectral measurements were performed with an MDR-2 monochromator with strobed photoelectronic recording.

Figure 14b shows the spectrum of the crystal under study in its geometry (following the notation of Porto) $z(yy, z+y)x$.[69] In other geometries the spectra also contain only two lines. The fact that this spectrum differs sharply from the RRS spectrum, obtained with close resonance conditions

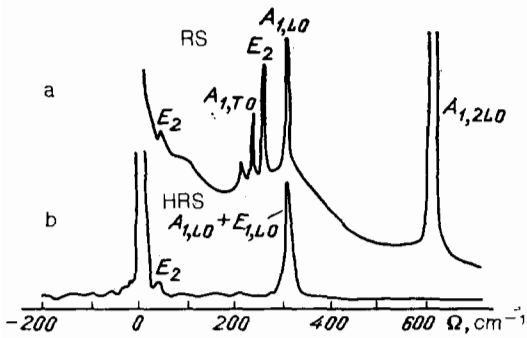


FIG. 14. The RRS spectrum (z, (y,y) x geometry) (a) and the RHRS spectrum (z $(yy, z+y)x$ geometry) of a CdS crystal. (From Ref. 69.)

of excitation (Fig. 14a), proves, in our opinion, that it belongs to RHRS.

The position of the long-wavelength limit of the absorption band of CdS ($2 \cdot 10^4$ cm^{-1} at 300 K) depends on the temperature: It shifts toward longer wavelengths as the temperature increases. This behavior was employed by Polivanov and Sayakhov in Ref. 14, and in addition they recorded a quadrupling of the integrated intensity of RHRS as the band limit approached the doubled energy of the excitation phonons ($2\hbar\omega_i = 18793$ cm^{-1}) as the temperature of the crystal was increased from 173 to 400 K. It was also observed that the relative intensity of the anti-Stokes component with a frequency of 305 cm^{-1} is higher than expected for the corresponding temperature of the sample, while the intensity of RHRS decreases from the quadratic dependence on the pumping field, and approaches saturation. In Refs. 14 and 67–69 these features were ascribed to the resonance conditions of excitation of the spectra: the increase in the intensity of RHRS was ascribed to the fact that the photon energies $2\hbar\omega_i$ and $\hbar\omega_s$ approach the actual absorption bands and the higher than theoretical intensity of the anti-Stokes component was ascribed to the fact that the resonance for it is sharper than that of the Stokes component (the third factor in the denominator of the expression (2.3)), while the tendency toward saturation was ascribed to the effect on the RHRS of the two-photon absorption of the scattered radiation in the field of the exciting radiation.

The vibrational representation for the optical modes of the CdS crystal, which has the form $\Gamma = A_1$ (RS, HRS, IR) + $2B_1$(HRS) + E_1(RS, HRS, IR) + $2E_2$(RS, HRS),[70] leads to the expectation that the HRS spectrum will contain eight lines (the dipole modes A_1 and E_1 split into LO and TO components). In the geometries of the experiment employed in Refs. 14 and 67–69, lines of both components with symmetry A_1 and E_1 as well as the modes B_1 and E_2 should be present in the HRS spectra. Nonetheless only the lines of the LO phonons with symmetry A_1 and E_1 (~ 305 cm^{-1}) and the line of the mode E_2 (~ 43 cm^{-1}) were observed in the RHRS spectra. The TO phonons and the line at the frequency $2\Omega_{LO}$ (the strongest line in the RRS spectrum; see Fig. 14a) could not be recorded, even when the sensitivity of the apparatus was increased by two orders of magnitude.

The fact that TO phonons are not present in the RHRS spectrum was attributed by the authors to the fact that the Fröhlich mechanism of electron-phonon interaction plays the dominant role in the scattering process, and the absence of a line at the frequency $2\Omega_{LO}$ is discussed on the basis of the excitonic nature of the electronic states that are important for RHRS and on the basis of the cascade mechanism of formation of scattering at the frequencies $n\Omega_{LO}$ by analogy to the model proposed in Ref. 71 for describing RRS in CdS. In this case the electronic states acquire a definite parity, and if RHRS at the frequency Ω_{LO} corresponds to the allowed two-phonon transition ($p \to s$), then at the frequency $2\Omega_{LO}$ it corresponds to the forbidden ($s \to s$) transition and it therefore is distinguished by low intensity. Based on the last assumption it should be expected that the maxima of the excitation spectra for RHRS should coincide with the position of the $2p$-level of the exciton. We note that if this model is correct, then H_{EL} should have an interband character.

In connection with the foregoing presentation, it is nat-

ural to study the results concerning the properties of RHRS spectra of ultradispersed bimodal mixed CdS_xSe_{1-x} crystals in a glass matrix,whose vibrational representation and selection rules are the same as those of CdS.[72] The smallness of the crystals (approximated by spheres), whose radii range from 12 to 50Å, depending on the composition and heat treatment, results in size quantization of the energy bands,[73] when out of all possible wave vectors of the electrons and holes only those satisfying the equality $k_{l,n} = \varphi_{l,n}/a$ are allowed, where $\varphi_{l,n}$ are the roots of the spherical Bessel function of order l and a is the radius of the particle. This results in the fact that in the absence of Coulomb interaction between the electron and the hole the absorption coefficient of a single sphere $K(\omega)$ is equal to

$$K(\omega) = A\sum_{l,n}(2l+1)\,\delta\left(\hbar\omega - E_g - \frac{\hbar^2 k_{l,n}^2}{2\mu}\right), \qquad (2.4)$$

where ω is the frequency of the light, E_g is the energy band gap in the macrocrystal, μ is the reduced mass of the electron and hole, and A is a constant.

Thus the bands decompose into a number of discrete levels and the particle acquires an atom-like absorption spectrum in which the lowest energy of the transition is shifted toward values higher than E_g. The size-dispersion of the particles, which is obtained when the particles are formed from the supersaturated solid solution in a glass silicate matrix, results in the fact that the absorption spectrum of real systems is inhomogeneously broadened. Light filters from the catalog of colored optical glasses with thermally induced coloration (OS-13 and -14 and KS-10, -11, and -14) were found to be suitable for investigating RRS and RHRS. Since the position of their absorption edge depends on the composition (Fig. 15) and frequency-tunable lasers are not available this raised hopes that it would be possible to obtain quite sharp resonances for both types of scattering spectra. At the same time the arbitrary orientation of ultradispersed particles in a matrix made it possible to obtain a complete collection of vibrational modes allowed for RRS and RHRS processes. The experimental apparatus and conditions are analogous to those employed in the investigation of adsorbed dyes (Sec. 2.2).

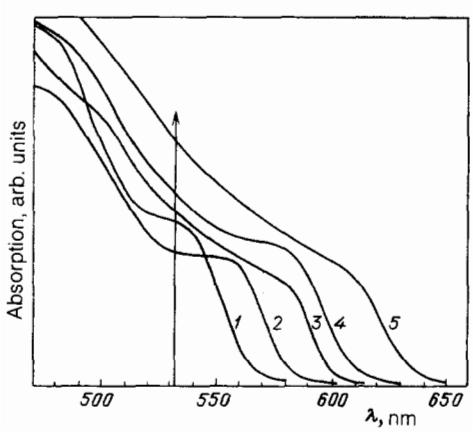


FIG. 15. The long-wavelength SPA edge of glasses containing CdS_xSe_{1-x} particles: *1–5*) OS-13 and -14 and KS-10, -11, and -14, respectively. The position of the doubled frequency of the exciting radiation is indicated.

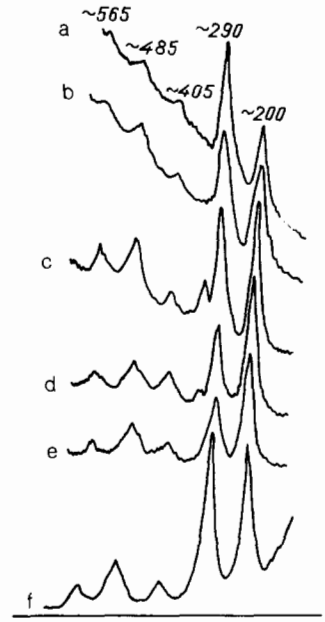


FIG. 16. a–e) the RHRS spectra of the glasses OS-13, -14, KS-10, -11, -14, respectively; the wavelength of the exciting light was equal to 1064 nm. f) RRS spectrum of KS-10 glass; the excitation wavelength was equal to 532 nm. The frequencies are given in cm^{-1}.

The RHRS spectra and, for comparison, the typical RRS spectrum of the glasses studied are presented in Fig. 16. For all systems it is evident that the frequencies and distribution of intensities are close and (with the exception of KS-10 and -11) the set of spectral lines is identical. In the latter two cases it was possible to record an additional line at ~ 325 cm^{-1}.

In agreement with Ref. 70 the lines at 200 and 290 cm^{-1} must be ascribed to LO phonons with $A_1(E_1)$ symmetry, and the high-frequency lines (~ 400, 490, and 570 cm^{-1}) must be ascribed to their overtones and combination vibrations, whose relative intensity, in contrast to the data of Ref. 71, is low and, as one can see, remains virtually constant from one sample to another. The lines which could be ascribed to TO phonons are not observed in either the RRS spectra or the RHRS spectra. This indicates that H_{EL} of Fröhlich type predominates in the scattering processes. The absence of the ~ 325 cm^{-1} line in the RRS spectra of CdS, CdSe, and CdS_xSe_{1-x} micro- and macrocrystals made it possible to ascribe it to a mode of B_1 symmetry, allowed by the selection rules only for HRS. Its appearance in the RHRS spectra of only two of the samples indicates that the excitation spectrum of RHRS by the B_1 mode is different from that by the LO component of the dipole mode $A_1(E_1)$. This could be caused by the predominance of H_{EL} of the deformation potential type in the scattering by the nondipole B_1 mode and (or) randomly realized conditions of sharp resonances with narrow excitation spectra, in contrast to the A_1 mode, which is observed for all samples.

The foregoing discussion shows that the excitation spectrum of RHRS contains fundamentally new information about its features. These features were first obtained by Watanabe and Inoue[74,75] in an investigation of a single crystal of $SrTiO_3$. This material was chosen because $SrTiO_3$ has been well studied by different methods, including also with the help of nonresonance HRS spectroscopy.[76,77] At the tem-

perature of the sample (120 K), used in Refs. 74 and 75, the $SrTiO_3$ crystal is in a cubic modification with the point symmetry group O_h, i.e., it is centrosymmetric. The optical vibrational representation has the form $\Gamma = 3F_{1u}$ (IR, HRS) $+ F_{2u}$ (HRS). The LO–TO splitting of the F_{1u} mode results in the appearance of seven lines in the HRS spectra. These lines were observed in the 90°-scattering geometry.[77] The LO phonons are forbidden in the backscattering geometry.[76] The limit of the energy gap lies near 3.46 eV.

The HRS spectra were obtained by excitation with pulsed dye-laser radiation (the pulse power $P \sim 15$ kW and the pulse repetition frequency $f \sim 20$ Hz) with the doubled photon energy $2\hbar\omega_i$, varied over the range 2.95–3.48 eV. The "forward"[74] and "backward"[75] scattering geometries were employed. The excitation spectra were measured with excitation pulses having constant power of about 10 kW and taking into account the spectral dependences of the index of refraction and the absorption coefficient in agreement with Ref. 65 as well as the spectral sensitivity of the entire system of instrumentation and the ω^4 law.

Figure 17 shows the spectrum of the preresonance HRS of the $SrTiO_3$ crystal. This spectrum was obtained in the "forward" geometry with $2\hbar\omega_i = 3.08$ eV. The inset in Fig. 17 shows the single-photon absorption spectrum of the crystal at a temperature of 121 K. Three optical modes TO-1, TO-2, and LO-3 (in the designation used in Ref. 74) as well as structure in the region ~ 1500 cm^{-1}, associated with the polariton mode, can be seen. Figures 18a and b show the excitation spectra of RHRS of TO-1 and LO-3 modes, respectively. It is obvious that the two excitation spectra differ in significant features: the intensity of RHRS by the TO mode grows monotonically as $2\hbar\omega_i$ approaches the limit of the energy gap, whereas RHRS by the LO mode remains virtually unchanged under preresonance conditions, when $2\hbar\omega_i < 3.3$ eV, and grows rapidly in the region $2\hbar\omega_i >$ 3.3 eV. In addition, special features are observed in both excitation spectra near 3.3 eV.

In the nonresonance HRS spectrum of the crystal, recorded in the "backscattering" geometry ($2\hbar\omega_i = 2.32$ eV),[75] the intensity of the LO-mode is very low compared with that of the TO-1 mode (Fig. 19a), but as $2\hbar\omega_i$ increases its intensity starts to increase at a leading rate (Fig. 19b); this is characteristic for resonance enhancement of the intensity of forbidden LO scattering, an effect that is well known

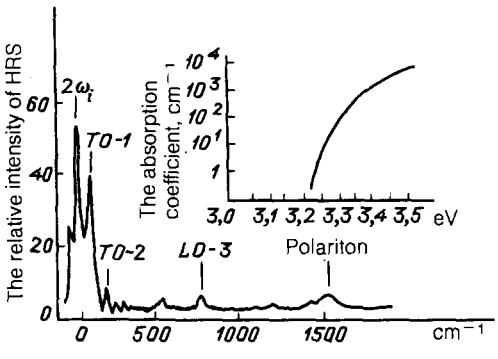


FIG. 17. The HRS spectrum of $SrTiO_3$ in the "forward" geometry; the excitation photon energy $2\hbar\omega_i = 3.08$ eV. Three optical and a polariton modes are marked. The SPA-spectrum of the crystal at 121 K is shown in the inset. (From Ref. 74.)

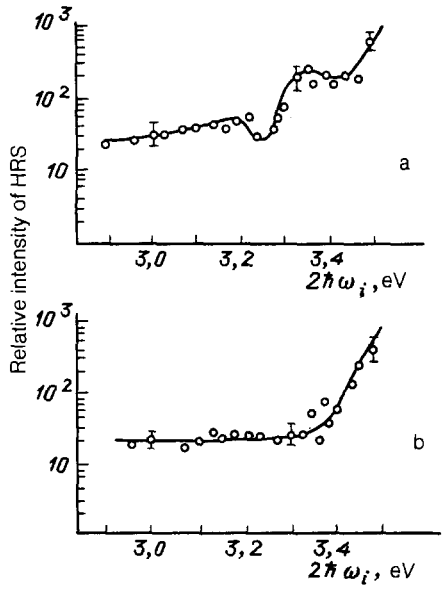


FIG. 18. HRS excitation spectra of $SrTiO_3$. a) TO-1 mode, b) LO-3 mode. The lines are drawn for convenience. (From Ref. 74.)

in the RRS spectroscopy of solids.[65] From the excitation spectrum of the RHRS by the LO-3 mode, presented in Fig. 20, one can see that as the band limit is approached the intensity of RHRS increases by up to a factor of $\sim 10^3$. In addition, the excitation spectrum contains a sharp feature near 3.05 eV. Finally, it was found that the intensity of RHRS by the LO-mode is virtually independent of the polarization of the exciting radiation, while in RRS the polarization of the forbidden LO-scattering is identical to the polarization of the exciting radiation.

To interpret the features of RHRS by the $SrTiO_3$ crystal in the "forward" scattering geometry (see Figs. 17 and 18) Watanabe and Inoue[74] proposed that the RHRS process proceeds according to the diagram shown in Fig. 13d. They start from the fact that in a centrosymmetric medium H_{EL} has an

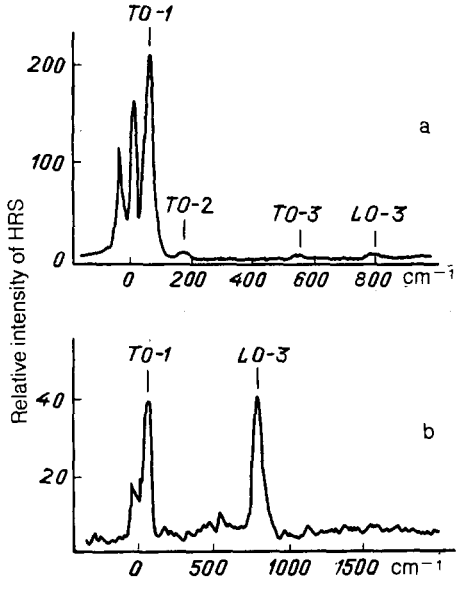


FIG. 19. The HRS spectra of $SrTiO_3$ in $z(xx, x+y)z$ geometry. a) Excitation with $2\hbar\omega_i = 2.32$ eV; b) excitation with $2\hbar\omega_i = 3.28$ eV. (From Ref.75.)

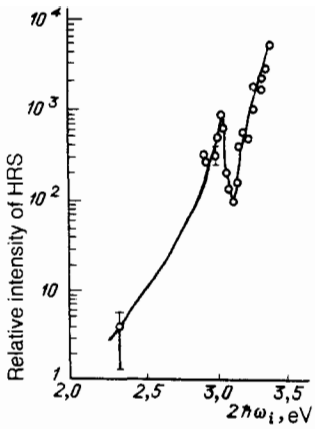


FIG. 20. HRS excitation spectra of $SrTiO_3$ on the LO-3 mode (From Ref. 75.)

interband character, and the hole contribution predominates because the region of the valence bands contains a band v_2 which has the appropriate symmetry, is split for the v_1 band by $\sim$ 1–2 eV, and could play the role of a quasiresonant intermediate state. The differences in the excitation spectra of RHRS by TO-1 and LO-3 modes are connected with the fact that for the former H_{EL} is of a deformation character while for the latter H_{EL} is of a Fröhlich character. Watanabe and Inoue[74] also make the assumption (generally speaking, not adequately substantiated) that the features observed in the excitation spectra of RHRS of both modes near 3.34 eV are determined by indirect transitions. This question, however, for the time being must be regarded as open.

The resonance enhancement of the intensity of RHRS by the LO-mode in a geometry, when it is forbidden for the nonresonance HRS (see Figs. 19 and 20), is compared in Ref. 75, by analogy to RRS, with the intraband H_{EL} of the Fröhlich type, i.e., with the process corresponding to the diagrams *a* and *b* in Fig. 13. But, since the $SrTiO_3$ crystal has a center of inversion, to remove the prohibition of transitions in RHRS it is proposed that at least one of the H_{EL} is a quadrupole interaction. Although it would be possible to explain on this basis the results of the polarization measurements, this assumption still seems to be doubtful: it is difficult to accept that the intensity of RHRS by the TO-mode is comparable to that of the LO-mode, for which a process of higher order is responsible. In Ref. 75 the possible scattering channels, including channels taking into account the presence of impurity levels as intermediate levels, are also studied. They can also determine the resonance features, mentioned above, in the region $\sim$3.05 eV. The final resolution of these questions requires further investigation.

In conclusion we shall briefly discuss two investigations where the RHRS spectrum of crystalline $LiTaO_3$ in its tetragonal phase was obtained.[78,79] Not only the results but also the particular features of the experiment themselves are of interest. Copper-vapor laser radiation at 578.2 and 510.6 nm was used for the first time to excite RHRS in the Stokes region. The spectra were observed in the region of the doubled frequency of the laser at the first wavelength and at the sum of the two frequencies with pulse power $P = 20$ kW and pulse repetition frequency $f = 8$ kHz. It is found that the recorded spectra differ from the RRS spectra only in that the intensity distribution is different.

CONCLUSIONS

The resonance-HRS spectroscopy is a new method for studying the vibrational and electronic structure of molecules and solids. In contradistinction to nonresonance HRS, this method yields information not only about molecular vibrations or phonon frequencies in solids but also about some parameters of the electronic transitions (single- or two-phonon transitions) with which the exciting radiation is in resonance.

This information can be extracted from RHRS spectra and, especially, from the excitation spectra of RHRS with the help of the vibronic theory of the process, in which the relation between the intermediate states active in the scattering and the intensities of the lines in the RHRS spectra was established. If, in particular, the excitation is performed in the region of the intense TPA band of the molecules, then predominantly the bands corresponding to the totally symmetric vibrations are intensified in the spectrum; when excitation is performed in the weak TPA band, coupled vibronically with the strong band, the bands of those nontotally symmetric vibrations which mix the corresponding electronically excited states will have the highest intensity.

The vibronic theory of RHRS by molecules was developed by analogy to the vibronic theory of RRS. A number of its conclusions (the fact that the bands of vibrations of some particular symmetry are predominantly intensified depending on the relative intensity of the active electronic transitions, the ratio of the intensities of the totally symmetric and nontotally symmetric vibrations, the bands of the first and second orders, etc.) are comparable to the results of the theory of RRS. Because of the different number of photons involved in the processes the results of the two theories differ significantly in a number of respects (antisymmetry of the tensors and selection rules).

The correctness of the theory of RHRS by molecules is confirmed by many examples of molecules in the gas phase and adsorbed on the surface of ultradispersed particles of silver. Experimental investigations have made it possible to obtain new information that could not be obtained by other methods.

There is still no theory of RHRS in solids, so that it is often difficult to interpret the RHRS bands and the corresponding excitation spectra. Nevertheless analysis of the experimental studies of RHRS in solids indicates that it may be possible to extract information about the types of vibrations in crystals, the parameters of the electronic states participating in the scattering, and the types of electron-phonon interactions. The successful development of RHRS spectroscopy here requires primarily the construction of an adequate theory of the process.

In spite of the fact that resonance conditions of excitation sharply increase the efficiency of the HRS process, the absolute intensities of the signals are very low and highly sensitive apparatus is required to record them. The optimal sources of excitation for systematic investigations are frequency-tunable sources in the visible and near-IR regions of the spectrum with relatively low pulse power, limited by the photochemical processes occurring in the samples, but with sufficiently high average power; this is achievable with high pulsed repetition frequencies. For luminescing objects, just as for RRS, the problem of discrimination of luminescence must be solved.

A great deal of information can now nonetheless be obtained by the RHRS method and further investigations in this direction should be expected. There is no doubt that RHRS will become an important method of investigation of the vibrational and electronic structure of molecules and solids.

[1] R. W. Terhune, P. D. Maker, and C. M. Savage, Phys. Rev. Lett. **14**, 681 (1965).
[2] S. J. Cyvin, J. E. Rauch, and J. C. Decius, J. Chem. Phys. **43**, 4083 (1965).
[3] J. H. Christie and D. J. Lockwood, *ibid.* **54**, 1141 (1971).
[4] V. N. Denisov, B. N. Mavrin, and V. B. Podobedov, Phys. Rep. **151**, 1 (1987).
[5] G. Placzek, "Rayleigh-Streuuing und Raman Effekt" in *Handbuch der Radiologie*, Akademische Verlagsgesellschaft, 1934, Vol. 6 [Russ. transl., Ukrainian State Scientific and Technical Publishing House, Kiev, 1934].
[6] A. C. Albrecht, J. Chem. Phys. **34**, 1476 (1961).
[7] J. Tang and A. C. Albrecht in *Raman Spectroscopy*, edited by H. A. Szymanski, N.Y., 1970, Vol. 2, p. 33.
[8] D. J. Kim and P. D. Koleman, IEEE J. Quantum Electron. **16**, 300 (1980).
[9] C. M. Savage and P. D. Maker, Appl. Opt. **10**, 219 (1971).
[10] J. Verdieck, S. H. Peterson, C. M. Savage, and P. D. Maker, Chem. Phys. Lett. **7**, 219 (1970).
[11] V. N. Denisov, B. N. Mavrin, V. B. Podobedov, and Kh. E. Sterin, Zh. Eksp. Teor. Fiz. **75**, 684 (1978); 84, 1266 (1983) [Sov. Phys. JETP **48**, 344 (1978); **57**, 723 (1983)].
[12] R. Chang and M. Long in *Light Scattering in Solids*, (Eds.) M. Cardona and G. Güntherodt, Springer-Verlag, N.Y., 1982, pp. 179–205 (Russ. transl., Mir, M., 1984).
[13] S. A. Akhmanov and D. N. Klyshko, Pis'ma Zh. Eksp. Teor. Fiz. **2**, 171 (1965) [JETP Lett. **2**, 108 (1965)].
[14] Yu. N. Polivanov and R. Sh. Sayakhov, *ibid.* **30**, 617 (1979) [JETP Lett. **30**, 580 (1979)].
[15] W. Heitler, *The Quantum Theory of Radiation*, Clarendon Press, Oxford, 1954 [Russ. transl., Inostr. lit., M. 1956].
[16] S. Kielich, *Molecular Nonlinear Optics* [Russ. transl. (from Polish), Miri, M., 1982].
[17] D. A. Long and L. Stanton, Proc. R. Soc. London A **318**, 441 (1970).
[18] V. I. Petrov., Opt. Spektrosk. **59**, 469 (1985) [Opt. Spectrosc. (USSR) **59**, 284 (1985)].
[19] V. I. Petrov, *ibid.*, 1315 [Opt. Spectrosc. (USSR) **59**, 788 (1985)].
[20] E. M. Verlan, *ibid.* **20** 605 (1966) [Opt. Spectrosc. (USSR) **20**, 341 (1966)].
[21] E. M. Verlan, *ibid.*, 802 [Opt. Spectrosc. (USSR) **20**, 447 (1966)].
[22] P. M. Champion, G. M. Korenowski, and A. C. Albrecht, Solid State Commun. **32**, 7 (1979).
[23] E. M. Verlan, Opt. Spektrosk. **20**, 916 (1966) [Opt. Spectrosc. (USSR) **20**, 508 (1966)].
[24] D. M. Friedrich and W. M. McClain, Ann. Rev. Phys. Chem. **31**, 559 (1980).
[25] L. Parma and N. Omenetto, Chem. Phys. Lett. **54**, 541 (1978).
[26] V. N. Denisov, B. N. Mavrin, V. B. Podobedov, and Kh. E. Sterin, Zh. Eksp. Teor. Fiz. **90**, 581 (1986) [Sov. Phys. JETP **63**, 338 (1986)].
[27] J. A. Koningstein and O. S. Mortenson, in *The Raman Effect* (Ed.) A.Anderson, Marcel Dekker, Inc. N.Y., 1973 pp. 519–542 [Russ. transl., Mir, M., 1977].
[28] Z. Ozgo, Wieloharmoniczne molecularne rozpraszanie swiatla wujeciu algebry Racacha, Poznan, 1975.
[29] M. Kozierowski, Z. Ozgo, and S. Kielich, J. Chem. Phys. **84**, 5271 (1986).
[30] P. D. Maker, Phys. Rev. A **1**, 923 (1970).
[31] L. D. Ziegler, Y. C. Chang, and Y. P. Zhang, J. Chem. Phys. **87**, 4498 (1987).
[32] R. N. Dixon, J. M. Bayley, and M. N. R. Ashfold, Chem. Phys. **84**, 21 (1984).
[33] F. Novak, J. M. Friedman, and P. Hochstrasser in *Laser and Coherence Spectroscopy*, (Ed.) J. I. Steinfeld, Plenum PRess, N.Y., 1978, pp. 451–518 [Russ. transl., Mir, M., 1982].
[34] Yu. T. Mazurenko, Opt. Spektrosk. **56**, 653 (1984) [Opt. Spectrosc. (USSR) **56**, 399 (1984)].
[35] L. D. Ziegler and J. L. Roeber, Chem. Phys. Lett. **136**, 377 (1987).
[36] J. S. Horwitz, B. E. Kohler, and T. A. Spriglenin, J. Phys. Chem. **89**, 1574 (1985).
[37] Y. C. Chung and L. D. Ziegler, *ibid.* **88**, 7287 (1988).
[38] Y. C. Chung and L. D. Ziegler, *ibid.*, 4692.
[39] L. D. Ziegler, *ibid.* **86**, 1703 (1987).
[40] A. V. Baranov and Ya. S. Bobovich, Pis'ma Zh. Eksp. Teor. Fiz. **36**, 277 (1982) [JETP Lett. **36**, 339 (1982)].
[41] A. V. Baranov, Ya. S. Bobovich, and V. I. Petrov, in *Abstracts of Reports at the Conference on Raman Scattering Spectroscopy* [in Russian], Krasnoyarsk, 1983, p. 273.
[42] A. V. Baranov, Ya. S. Bobovich, and V. I. Petrov, in *Abstracts of Reports at the 19th All-Union Conference on Spectroscopy*, Tomsk, 1983, Part IV, p. 134.
[43] A. V. Baranov, Ya. S. Bobovich, V.N. Denisov *et al.*, Opt. Spektrosk. **56**, 580 (1984) [Opt. Spectrosc. (USSR) **56**, 355 (1984)].
[44] A. V. Baranov, Ya. S. Bobovich, and V. I. Petrov, *ibid.* **58**, 578 (1985) [Opt. Spectrosc. (USSR) **58**, 353 (1985)].
[45] A. V. Baranov, Ya. S. Bobovich, and V. I. Petrov, Zh. Eksp. Teor. Fiz. **88**, 741 (1985) [Sov. Phys. JETP **88**, 435 (1985)].
[46] A. V. Baranov, Ya. S. Bobovich, and V. I. Petrov, Opt. Spektrosk. **61**, 505 (1986) [Opt. Spectrosc. (USSR) **61**, 315 (1986)].
[47] A. V. Baranov, Ya. S. Bobovich, and N. P. Vasilenko, *ibid.*, 780 [Opt. Spectrosc. (USSR) **61**, 490 (1986)].
[48] A. V. Baranov and S. V. Popov, Zh. Prikl. Spektrosk. **50**, 764 (1989) [J. Appl. Spectrosc. (USSR) **50**, 487 (1989)].
[49] A. V. Baranov and Ya. S. Bobovich, Opt. Spektrosk. **52**, 385 (1982) [Opt. Spectrosc. (USSR) **52**, 231 (1982)].
[50] R. K. Chang and T. E. Furtak [Eds.], Surface-Enhanced Raman Scattering, Plenum Press, N.Y., 1982 [Russ. transl., Mir, M., 1984].
[51] A. Otto, in *Light Scattering in Solids IV*, (Eds.) M. Cardona and G. Güntherodt, Springer-Verlag, N.Y., 1984.
[52] A. V. Baranov, Ya. S. Bobovich, and V. I. Petrov, Opt. Spektrosk. **61**, 992 (1986) [Opt. Spectrosc. (USSR) **61**, 620 (1986)].
[53] J. A. Creighton, in Ref. 50, pp. 315–337.
[54] T. N. Smirnova, E. A. Tikhonov, and M. T. Shpak, Pis'ma Zh. Eksp. Teor. Fiz. **29**, 453 (1979) [JETP Lett. **29**, 411 (1979)].
[55] B. Foucault and J. P. Hermann, Opt. Commun. **15**, 412 (1975).
[56] A. A. Aristov, V. G. Maslov, S. G. Semenov, and V. S. Shevandin, Izv. Akad. **18**, 569, Nauk SSSR, Ser. Fiz. **44**, 750 (1980) [Bull. Acad. Sci. USSR, Phys. Ser. **44**(4), 55(1980)]; Teor. Eksp. Khim. **18**, 619 (1982) Theor, Exp. Chem. USSR (1982); Khim. Fiz. **11**, 1592 (1983) [Sov. J. Chem. Phys. (1983)].
[57] J. P. Hermann and J. Ducuing, Opt. Commun. **6**, 101 (1972).
[58] V. L. Ermolaev and V. A. Lyubimtsev, Tr. Gos. Opt. Inst. **65**, 20 (1987).
[59] H. Kuhn, Fortschr. Chem. Org. Naturstoffe **17**, 404 (1959).
[60] F. P. Shäfer [Ed.], Dye Lasers, Springer-Verlag, Berlin, 1974. [Russ. transl., Mir, M., 1976].
[61] M. V. Melishchuk, V. I. Prokhorenko, G. G. Dyadyusha *et al.*, "*Polymethine dyes for passive Q-switching*" (In Russian), Preprint No. 60, Institute of Physics of the Academy of Sciences of the Ukr. SSR, Kiev, 1986.
[62] A. V. Baranov, A. V. Veniaminov, and V. I. Petrov, Zh. Prikl. Spektrosk. **44**, 59 (1986) [J. Appl. Spectrosc. (USSR)**44**, 46 (1986)].
[63] E. A. Gastilovich, K. V. Tskhai, and D. N. Shigorin, Opt. Spektrosk. **41**, 566 (1976) [Opt. Spectrosc. (USSR) **41**, 332 (1976)].
[64] S. S. Jha and J. W. F. Woo, Nuovo Cimento B **2**, 164 (1979).
[65] M. Cardona, in Ref. 12, pp. 19–178.
[66] R. M. Martin and L. M. Falikov, in *Light Scatteirng in Solids*, (Eds.) M. Cardona, and G. Güntherodt, Springer-Verlag, N.Y. (1975), pp. 80–145 [Russ. transl., Mir, M., 1979].
[67] Yu. N. Polivanov and R. Sh. Sayakhov, Krat. Soobshch. Fiz., No. 8, 31 (1979) [Sov. Phys. Lebedev Inst. Rep. No. 8, 26 (1979)].
[68] Yu. N. Polivanov and R. Sh. Sayakhov, Kvant. Elektron. **6**, 2485 (1979) [Sov. J. Quantum Electron. **9**(11), 1472 (1979)].
[69] R. Sh. Sayakhov, Tr. IOFAN **2**, 56 (1986).
[70] G. R. Wilkinson, in Ref. 27, pp. 811–983.
[71] A. A. Klochikhin, S. A. Permogorov, and A. N. Reznitskiĭ, Zh. Eksp. Teor. Fiz. **71**, 2230 (1976) [Sov. Phys. JETP **44**, 1176 (1976)].
[72] A. V. Baranov, Ya. S. Bobovich, N. I. Grebinshchikova, V. I. Petrov, and M. Ya. Tsenter, Opt. Spektrosk. **60**, 1108 (1986) [Opt. Spectrosc. (USSR) **60**, 685 (1986)].
[73] Al. L. Efros and A. L. Efros, Fiz. Tekh. Poluprovodn. **16**, 1209 (1982) [Sov. Phys. Semicond. **16**, 772 (1982)].
[74] K. Watanabe and K. Inoue, J. Phys. Soc. Jpn. **59**, 726 (1989).
[75] K. Inoue and K. Watanabe, Phys. Rev. B **39**, 1977 (1989).
[76] K. Inoue, N. Asai, and T. Sameshima, J. Phys. Soc. Jpn. **50**, 1291 (1981).
[77] H. Vogr and G. Heumann, Phys. Status Solidi B **92**, 56 (1979).
[78] A. M. Agal'tsov, V. S. Gorelik, and M. M. Sushchinskiĭ in Ref. 41, p. 42.
[79] A. M. Agal'tsov, V. S. Gorelik, and M. M. Sushchinskiĭ, Opt. Spektrosk. **58**, 386 (1985) [Opt. Spectrosc. (USSR) **58**, 230 (1985)].

Translated by M. E. Alferieff