Resonance inelastic three-photon scattering: physical model and experimental results

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A method is developed for obtaining the inelastic three-photon scattering resonance spectra (TPS) in very dilute eye solutions ($\sim 10^{-6}$ M). The method is based on the strong enhancement of the scattered radiation by molecules adsorbed on colloid silver particles. A large number of dyes of various classes are investigated by the technique proposed, e.g., rhodamines, pyronines, thioindigos, etc. The vibronic theory of ordinary (two-photon) resonance combination scattering is extended to the case of TPS. This has permitted the totally symmetric vibrations to be separated from certain types of incompletely symmetric vibrations, and therefore to derive the rules determining the intensities of the resonance inelastic TPS lines. A number of general spectral laws are interpreted qualitatively on the basis of the theory. It is pointed out that for further development of the method and its structural applications, measurement of the TPS, excitation profiles and of two-photon absorption of dyes should be useful.

1. INTRODUCTION

From the quantum viewpoint, the inelastic three-photon scattering (TPS), also called hyper-Raman scattering in the literature, represents a process of interaction of radiation with the medium in which two ω photons of this radiation disappear and a new $2\omega \pm \omega_{\text{med}}$ photon is created. Here ω_{med} is one of the characteristic frequencies of the medium, for example, the frequency vibrational motion of the atoms or ions forming it.[1]

The three-photon character of the process is responsible for its extraordinarily low efficiency. According to approximate estimates for typical light fields, the inelastic TPS is lowered in intensity by a factor of 10^6 relative to ordinary (two-photon) Raman scattering. Therefore, a special high-sensitivity apparatus is necessary for its observation.[2] Numerous investigations of TPS in transparent media have been carried out to date in states.[1] In recent years, important results have been obtained, in particular, relating to the problem of the glasslike state of matter and in the general sense, the physics of condensed matter.[3–8]

The cross section of inelastic TPS can be significantly increased by using resonance conditions to excite it. Their role has been discussed theoretically on several occasions.[9–11] The possibility of producing a double resonance, in which the incident radiation resonates with the one-photon and two-photon transitions in the absorption, has also received attention. So far as the experimental results of researches on this theme are concerned, we know of only one publication, the authors of which evidently succeeded in producing a comparatively small (less than fourfold) change in the intensity of the principal line of inelastic TPS in a CdS crystal in the case of a temperature shift in the boundary of its absorption.[12]

Interest in the resonance inelastic TPS stems not only from the need to intensify the spectra, i.e., by purely methodological considerations, but also by the fact that in this process (as also in resonance Raman scattering), the properties of the electron-excited states stand out especially clearly. At the same time, spectra become more informative. However, to realize this advantage, it is necessary to develop and validate the method of obtaining them, and to establish the basis of the physical approach to their interpretation.

The present work improves on the preliminary results stated earlier[13] by systematically investigating the resonance inelastic TPS of a large group of various dyes adsorbed on particles of colloidal silver, i.e., in the so-called giant amplification regime. In the choice of this method, we started out from the viewpoint that it should guarantee a significant increase in the scattered radiation and at the same time radically decrease in the luminescence background which, as is well known, frequently masks the weak scattering lines. In every case, in our investigation of the resonance giant Raman scattering, the present method completely satisfied these two conditions,[14] and at the same time allowed us to obtain spectra from very dilute solutions ($\sim 10^{-9}$M).

In order that the silver hydrosol not contain secondary products, it was made by reducing the silver oxide with hydrogen in an aqueous medium,[14] rather than by means of complicated reagents as has been done by others. According to the data obtained from electron microscopy and small-angle x-ray scattering, the silver particles had spherical shape and a diameter of about 30 nm. The inelastic TPS spectra were excited by radiation with a wavelength of 1064 nm from a high-frequency pulsed YAG:Nd^{+3} LTI-502 laser (peak power up to 10 kW pulse rate 10 KHz). The Raman scattering necessary for comparison with the resonance spectra was excited by the second harmonic of the radiation from this laser or by an argon laser. The spectral apparatus was DFS-24 with the usual recording.

Rhodamines, pyronines, acridine orange, thioindigos, peryline, pyrilic sol, parafuchsin and crystalline violet were studied. The thioindigos, peryline and pyrilic sol were introduced into the hydrosol by means of an intermediate solvent—acetone or pyridine. Typical concentrations of the dyes amounted to 10^{-6} mol.

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We set out to study the principal spectroscopic features of the resonance inelastic TPS of these materials, and also to interpret the results qualitatively with the help of familiar physical models of linear and nonlinear radiation matter interaction and of the structure of the scattering molecules themselves. Here we have used well-established data on two-photon absorption (TPA) of certain dyes dissolved in ordinary liquids in the absence of silver particles. The appropriateness of this simplification is established *a posteriori* from the description and discussion of the results. We have ignored the question of the causes and mechanisms of giant amplification of the scattering spectra for molecules adsorbed on silver particles.

2. THEORETICAL CONSIDERATION

A variant of the quantum theory of resonance Raman scattering has achieved currency in the past two decades. This method allows us to explain a number of important spectral features.[15,16] The physical idea at the base of this variant lies in the synthesis of representations of vibronic spectroscopy on the mixture of different electron states by means of certain totally symmetric vibrational coordinates, on the one hand, and the quantum theory of scattering on the other. The complete eigenfunction is written down in the adiabatic approximation. The coefficient of the Herzberg-Teller interaction h_a of the levels is introduced directly into the expression for the matrix element of polarizability. As a result, it decomposed into three terms (A, B, and C, in the notation of Refs. 15 and 16). The first term ($A \sim k_e \Delta_e$, where k_e is the force constant, Δ_e is the shift in the equilibrium value of the nuclear coordinates associated with electron excitation) with a stronger frequency dependence describes the intensity of the fully symmetrized coordinates, the second term ($B \sim h_a$) describes those nontotally symmetric vibrations that assure the mixing. Finally, the third term (C) furnishes the interaction of the ground state with the electronically excited states and in most cases can be neglected. Preferential amplification of nontotally symmetric oscillations, active in the mixture, corresponds to the situation in which the excitation is carried out within the weak absorption band and extracts intensity from the strong band.

We now consider how much this model, which allows us to separate in a transparent way the nontotally symmetric oscillations from the totally symmetric, can be generalized to the case of resonance inelastic TPS, similar to what is down in Ref. 11 for the semiclassical Placzek theory.

In accord with the results of Ref. 11, the Raman hyperpolarizability of second order is equal to

$$(\beta_{\rho\sigma\tau})_{nk} = \frac{2}{\hbar^2}\sum_{r,s}\Big[\frac{M_{nr}{}^{\sigma}M_{rs}{}^{\rho}M_{sk}{}^{\tau}}{(\omega_{sk}-\omega-i\Gamma_{sk})(\omega_{rn}+\omega-i\Gamma_{rn})} + \frac{M_{nr}{}^{\sigma}M_{rs}{}^{\tau}M_{sk}{}^{\rho}}{(\omega_{sn}+2\omega-i\Gamma_{sn})(\omega_{rn}+\omega-i\Gamma_{rn})} + \frac{M_{ns}{}^{\rho}M_{sr}{}^{\sigma}M_{rk}{}^{\tau}}{(\omega_{sk}-2\omega-i\Gamma_{sk})(\omega_{rk}-\omega-i\Gamma_{rk})}\Big], \tag{1}$$

where $\mathbf{M}_{ij}$ is the matrix element of the dipole moment, constructed from the complete wave functions i and j of the initial (k), final (n) and intermediate (r,s) states $\mu\,\rho, \sigma, \tau = x, y, z$; Γ_{ij} and ω_{ij} are the width and difference in frequencies of the transitions between the state i and j, and ω is the frequency of the exciting light.

We are interested in the resonance of the pump frequency with the long wavelength band of two-photon absorption of the molecule (the third component in Eq. (1)). Applying the adiabatic approximation and the expansion of the electron wave function in a Taylor's series in the normal coordinates (the Herzberg-Teller expansion) we have for the second order hyperpolarizability

$$(\beta_{\rho\sigma\tau})_{g0,\,gj} = A + B, \tag{2}$$

$$A = \sum_{e\neq g}\sum_{v}\Big[\frac{(g^0|M_\rho|f^0)(f^0|M_\sigma|e^0)(e^0|M_\tau|g^0)}{(E_{ev,g0}-2E_0)(E_{f0}-E_{g0}-E_0)}\Big]\langle 0|v\rangle\langle v|j\rangle \tag{3}$$

$$B = \sum_{e\neq g}\sum_{v}\sum_{s\neq e}\sum_{a}\Big\{\Big[\frac{(g^0|M_\rho|f^0)(f^0|M_\sigma|e^0)(e^0|h_a|s^0)(s^0|M_\tau|g^0)}{(E_{ev,g0}-2E_0)(E_{f0}-E_{g0}-E_0)}\Big]\frac{\langle 0|v\rangle\langle v|Q_a|j\rangle}{E_{e0}-E_{s0}} + \Big[\frac{(g^0|M_\rho|f^0)(f^0|M_\sigma|s^0)(s^0|h_a|e^0)(e^0|M_\tau|g^0)}{(E_{ev,g0}-2E_0)(E_{f0}-E_{g0}-E_0)}\Big]\frac{\langle 0|Q_a|v\rangle\langle v|j\rangle}{E_{e0}-E_{s0}}\Big\}, \tag{4}$$

where $|g^0)$ is the electron wave function of the ground state, $|f^0)$, $|e^0)$, $|s^0)$ are the electron wave functions of the intermediate states, $M_{\rho,\sigma,\tau}$ are the (x, y, z) components of the dipole moment, $h_a = (\partial\mathscr{H}/\partial Q_a)_0$ is the operator of vibronic coupling, $E_{ev,g0} = E_{ev} - E_{g0}$ is the energy difference between the vibronic states, $E_{e0} - E_{s0}$ is the energy difference of the electronic states $|e^0)$ and $|s^0)$, $E = \hbar\omega$, Q_a is the normal coordinate of the $v = a$ oscillation. In (2), the summation over the vibronic states Σ_{ij} is replaced by a single non resonant electron level $|f^0)$. For brevity of notation, components that do not experience resonance at $2E_0 \to E_{e0}$ are omitted. The term C is also neglected.

The role of the vibrational structure of the two-photon absorption band can be taken into account with the help of the approximate expansion[11]

$$\sum_{v}\frac{\langle 0|v\rangle\langle v|j\rangle}{E_{ev,g0}-2E_0} \approx \sum_{a}\frac{(e^0|h_a|e^0)Q_a}{(E_{e0}-E_{g0}-2E_0)^2}. \tag{5}$$

Here the term A transforms into

$$A'' = \sum_{e}\sum_{a}\Big[\frac{(g^0|M_\rho|f^0)(f^0|M_\sigma|e^0)(e^0|M_\tau|g^0)}{(E_{e0}-E_{g0}-2E_0)^2(E_{f0}-E_{g0}-E_0)}\Big](e^0|h_a|e^0)\langle 0|Q_a|j\rangle, \tag{6}$$

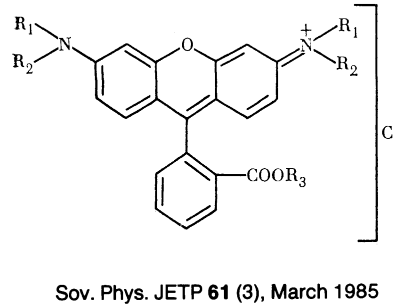
where $(e_0|h_a|e_0) = k_e\Delta$.

It follows from this analysis that the resonance inelastic TPS is described by expressions with the same structure as the resonance Raman scattering. Within the framework of this representation, it is important to distinguish two experimental situations—the excitation of spectra inside the weak and inside the strong band of two-photon absorption, which describe transitions between the ground and the mixed states. In the first case, the incompletely symmetrized oscillations that are active in the mixture are amplified abruptly and selectively. This can in principle only impoverish the lines of the spectrum of resonance TPS in comparison with spectra excited in the region of transparency of the material. If the second case occurs, i.e., if the excitation is carried out inside or near the strong two-photon absorption band, then lines of the completely symmetrized oscillations for all molecules with the exception of those which have a center of inversion or relate to the groups D_4, D_{5h}, and D_{id} will dominate in the spectra of resonant TPS. The reason for this is that the totally symmetric oscillations are forbidden for them by the selection rules[17]. Under similar conditions, we can expect these spectra to be quite similar to those of resonant Raman scattering. Finally, if the exciting radiation falls between the weak and strong two-photon absorption bands, then interference of the scattering amplitudes is possible, similar to that observed in the resonant Raman scattering, including interference of a destructive character.[18] Therefore studies of the spectra of excitation of resonance inelastic TPS are very important. However, at the present time, lasers that are suitable for this approach are lacking.

Thus, the correct interpretation of the experimental material on resonance TPS and Raman scattering, considered jointly, and which allow us to draw basic structural conclusions, becomes possible if not only the selection rules are applied, but also the intensity rules for the corresponding spectral lines. The latter rules can be studied for example with the help of the expressions set forth above, but under the condition that the spectra of the two-photon absorption of the investigated molecules are known. However, there is, unfortunately, only meager information in the literature on this subject. In such a situation, the systematic investigation of the two-photon absorption in dyes represents a very urgent problem both in order to clarify the general laws of the process of resonance inelastic TPS, and also in connection with its structural application.

3. DESCRIPTION AND DISCUSSION OF THE EXPERIMENTAL RESULTS

Rhodamines and related compounds. A xanthenic fragment and a benzol radical with substitutions enter into the composition of rhodamine dyes. Their general structural formula has the form



where $R_{1,2} = H, CH_3, C_2H_5$; $R_3 = H, C_2H_5$. In one of the members we have studied of this class of dyes, the aliaphatic group $(CH_2)_2COOH$ enters instead of the benzol radical, while in the pyronines, the benzol radical with substitution is replaced by a hydrogen atom. Therefore, it makes sense to study dyes of both types simultaneously.

As is shown in Ref. 19, the presence of the carboxyphenyl group in rhodamines does not have a significant effect on the π-electron system of the xanthene skeleton. This is connected with the fact that the planes of both fragments are mutually perpendicular and, consequently, they do not form a common conjugate bond. The latter implies that the oscillations of the atoms of the carboxyphenyl group will not experience resonance amplification and do not appear in the scattering spectra.

Further information on the structure and symmetry of electronic transitions in rhodamines can be obtained from polarization spectra of the one- and two-photon absorption.[20,21] In particular, it was shown in Ref. 20 that the ground state S_0 and the first excited state S_1 in rhodamines have opposite symmetry and that the dipole moment of the long wave transition lies in the yz plane of the xanthene fragment, which has C_{2v} symmetry, and whose length is directed along the y axis connecting the amino groups. Since the ground state is completely symmetric (A_1), it is necessary to ascribe the symmetry B_2 to the first excited state S_1. At the same time, the symmetry of the second excited state S_2 is the same as that of the first (A_1). According to direct measurements of the two-photon absorption spectra of rhodamines 110 and 6G (Ref. 22), the ${}^1A_1 \rightarrow {}^1B_2$ transition is very weak and is resolved mainly by the nontotally symmetric oscillations of symmetry b_2. This indicates that the symmetry of the xanthene skeleton is conserved in them for all rhodamines. The two-photon transition to the state S_2, according to the data of Ref. 20, on the other hand, is resolved and is characterized by a significantly larger cross section.

We have obtained the spectra of resonant inelastic TPS and resonance Raman scattering under the same giant amplification conditions. Before entering on a description and the possible interpretation of the results of the investigation of these (and other) materials, let us make two observations of a methodological character. The first pertains to the use in our experimental situation of data on the absorption of rhodamines in ordinary solutions, i.e., those not containing silver particles. It seems to us, this is justified by the fact that the excitation spectra of resonance Raman scattering of rhodamines, adsorbed on the silver, reproduce their intense long wave band of single-photon absorption in the pure solution[23]. In those dyes of another class (for example, in parafuchsin and crystalline violet), which it has been possible to investigate not only in silver hydrosol, but also in pure water solution, the spectra of resonant Raman scattering (ordinary and enhanced) are found to be completely identical. All this shows that the adsorption of dyes by silver particles takes place according to a physical mechanism little related to the electron and especially the nuclear structure of the molecules. Further, since the accuracy of the frequency of the lines can be measured amounts to a quantity of about 2 cm^{-1}, in the spectra of resonance TPS and Raman scattering

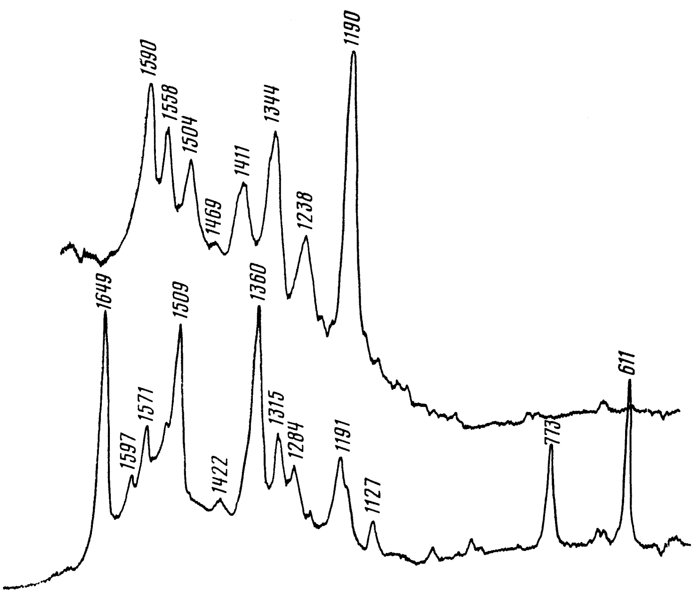


FIG. 1. Spectra of resonance TPS (upper) and Raman scattering (lower) of rhodamine 3B. Here (and later in Figs. 2–5), the excitation was created by radiation with wavelengths of 1064 nm and 532 nm, respectively. The line frequencies are shown in cm^{-1}.

being compared, we refer to lines with different types of oscillations if the difference in their frequency is not less than 4 cm^{-1}.

The similar structure of rhodamine and pyronine dyes makes their resonance Raman scattering spectra quite similar: a number of lines coincide, for each of which is found an analog which is close in frequency in the spectra of other dyes and the various relative intensities differ little. The same parallel is revealed in the resonance spectra of TPS and Raman scattering in the region of frequencies above 1000 cm^{-1}. However, a comparison of the spectra of both types for each of the investigated dyes shows their essential difference. In particular, this refers to the rhodamines Zh, 6Zh, 3B "semi-B" and 110, for which the presence in the spectra of both types of only one common line is characteristic. In the spectra of rhodamines B and S, two and three lines, respectively, are identical in frequency. The resonances of Raman scattering and TPS in rhodamine S, pyronines B and Zh and acridine red are distinguished by a marked similarity.

Let us illustrate what has been said above by examples. For this, we show the spectra of rhodamine 3B in Fig. 1. It is seen that in general for both spectra there is one intense line of 1190 cm^{-1}. Both rhodamine 6Zh spectra are shown in Ref. 13, but in Ref. 24, similar data are tabulated for one additional representative of this group of dyes—rhodamine G. We also note that the discrepancy in the frequencies of the lines in the resonance spectra of Raman scattering and TPS of rhodamines G and 6G extends also to the region of over-

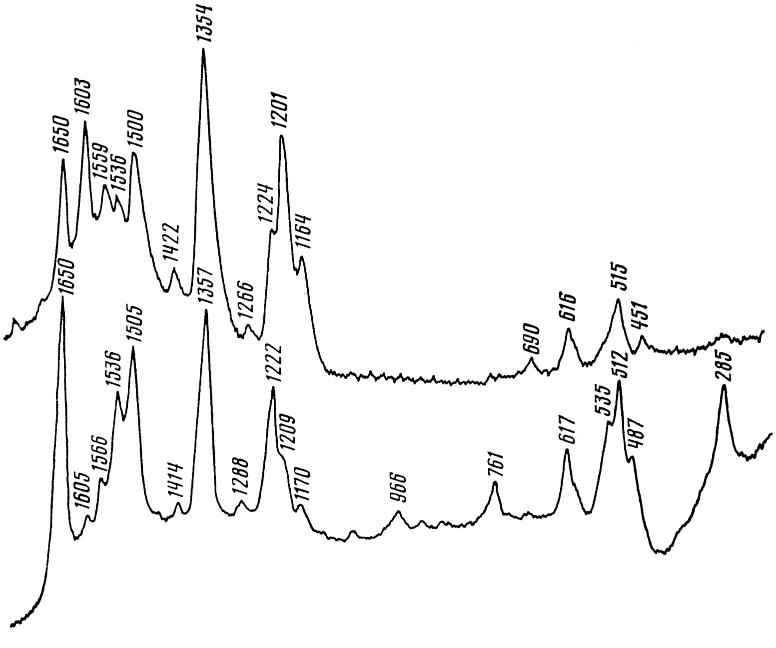


FIG. 2. Spectra of resonance TPS (upper) and Raman scattering (lower) of rhodamine S.

tones and compound oscillations.[24] The situation is different in the case of the spectrum of rhodamine S, shown in Fig. 2: here, within the limits of the given criterion, many of the lines are coincident in frequency. Such a picture is observed in the spectra of pyronines B and Zh and acridine red, but for them, the presence in the TPS spectrum of intense lines with frequencies less than 1150 cm^{-1} is still characteristic, and also the line 1650 cm^{-1}, which is evidently related to the completely symmetric oscillations of the $C = C$ bond of the xanthene skeleton.[25]

The fact that the spectra of resonant TPS in these compounds differ altogether in intensity is worthy of attention. The weakest spectra were the rhodamines "semi-B" and 110 which could be recorded only with the help of high-sensitivity apparatus.[1)]

It is possible to explain the basic law qualitatively, starting from the concept of the vibronic nature of Raman scattering. According to Refs. 15 and 16, the resonance with the intense long wavelength single-photon absorption band ($B_{\max} \sim 530$ nm) leads to a preferential enhancement of the completely symmetrized oscillations (a_1) in the spectra of ordinary Raman scattering. However, the intense two-photon absorption of the rhodamines is found in the $S_0 \rightarrow S_2$ region ($\lambda \sim 350$ nm)[20], while the weak two-photon absorption band $S_0 \rightarrow S_1$, with a cross section which is smaller by two orders of magnitude, falls in the excitation region. In accord with the generalized scattering theory (see above), this circumstance should, on the other hand, guarantee the selective enhancement of these incompletely symmetrized oscillations, which most actively mix the states S_1 and S_2 of the rhodamines. Since the transition moments $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ are directed along the y and z axes, in the present case, oscillations of the type $b_2(B_2(y) \times b_2 = A_1(z))$, will be mixtures. These oscillations appear in the spectra of resonant TPS.

The last assertion is valid if in the excitation, the symmetry of the xanthene skeleton is preserved, which is possibly helped by the presence of the carboxyphenyl group, the electron properties of which increase the density of π-electrons close to the amino groups in the excited state S_1 and decrease their mobility.[26] The absence of this group of rhodamine S, pyronines and acridine red may be the reason for the fact that the plane of the xanthene skeleton becomes less rigid. In agreement with the existing theoretical concepts,[27] several oscillations of symmetry a_3 should be activated in the Raman scattering here, and in the TPS spectra—oscillations of the symmetry b_1. This is comparable with the decrease in the symmetry of the excited state, at least up to C_2.

The activation of "low-frequency" vibrations, observed experimentally and noted above, especially in the TPS spectra of pyronines, confirms this assumption. On the other hand, the appearance in the TPS spectra of these compounds of rather intense lines at 1650 cm^{-1} indicates some enhancement of the totally symmetric oscillations. This can be ascribed to the increase in the relative role of the A term in the process of scattering, if the probable interference of the contributions to the intensity from the A and B terms leads to antiresonance.[18]

The weakness of the TPS spectra (for example, rhodamine 110) is most readily explained as follows. As shown by direct measurements in Ref. 22, in comparison with rhodamines 6G, the long wave two-photon absorption band in this case is shifted to shorter wavelengths, as a result of which the exciting radiation will no longer exhibit a sharp resonance. On the other hand, the conditions for rhodamine 6G are favorable in this sense.

Acridine orange. In contrast with what was considered above, this dye contains N and not O as the heteroatom. Both types of spectra contain the same set of lines with relatively similar intensities (Fig. 3). Just as in pyronine, low-frequency vibrations are well represented in its spectra and also vibrations of the $C = C$ bond (1643 cm^{-1}). The coinci-

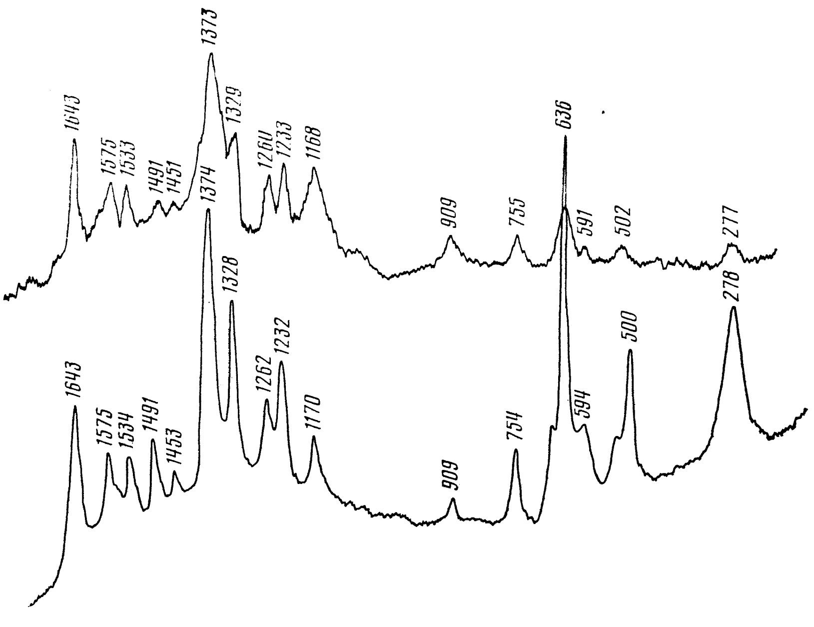
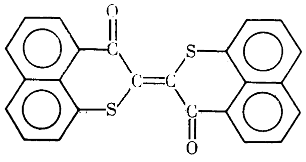


FIG. 3. Spectra of resonance TPS (upper) and Raman scattering (lower) of acridine orange.

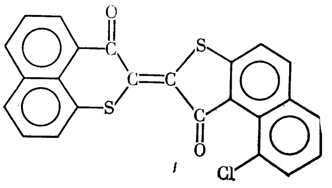
dence of line frequencies could be explained by starting out from the assumption that the molecules of this dye lack all the nontrivial elements of symmetry, as a consequence of which the selection rules for the vibrations lose significance. However, among the resonance spectra of the Raman scattering of pyronines and acridine orange, there are many signs of similarity. Therefore, without excluding several differences of symmetry of the chromofor from $C_{2\sigma}$, it is necessary to assume that they are not decisive, and the coincidence of the frequencies should find some other explanation.

The compared materials differ in one significant aspect: as follows from the results of measurement of the cross sections of two-photon absorption for light with linear and circular polarization,[21] the S_0 and S_1 states of acridine orange have the same symmetry. Therefore, the $S_0 \rightarrow S_1$ transition in two-photon absorption is highly permitted, and the two-photon absorption cross section is large. Moreover the transition is intense even with ordinary absorption. The consistency of these data is shown in Ref. 21 on the basis of quantum chemical analysis and by accounting for the contributions of the different electron configurations to the state S_1. Within the context of the problem that we have addressed ourselves to, it is important that, in the case of acridine orange, one and the same state be present for resonance Raman scattering and TPS, which guarantees the preferential enhancement of the totally symmetric vibrations in spectra of both types, and consequently, the identity of the latter which we have observed is explained.

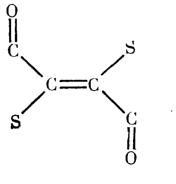
Thioindigos. These dyes exist in cis- and trans-forms, as noted in Ref. 28, which are determined by the configurations of the principal chromoforic groupings of the atoms, and not by the molecules as a whole, and which have symmetry C_{2v} and C_{2h}, respectively. The structure of the more stable trans-isomers of the two dyes of this type, which we have studied in more detail than the others, are represented by the following formulas:



and



where the chromoforic grouping in question has the following form:



Since the dyes are photochromic, the possibility arises of using an additional laser to alter the concentration of one or another isomer in the process of recording the TPS spectra. Without going into experimental details, we only note that the affiliation of the obtained spectra of resonance TPS with the cis-isomers of these dyes is established in such a way. Although we have studied a rather large number of representatives of the given class of dyes, in no case have we succeeded in obtaining the spectrum of resonance TPS of trans-isomers, in spite of the favorable conditions of resonance excitation.

As is seen from Eq. (1) for the quadratic hyperpolarizability, the products of matrix elements of the type $\mathbf{M}_{ns} \times \mathbf{M}_{sr} \times \mathbf{M}_{rk}$, enter into its numerator. Here k is the index of the vibronic function of the ground state, n of the final and r, s, of intermediate states. In the adiabatic approximation, this product is formed of matrix elements constructed from the corresponding electronic wave functions. Since the initial and final electronic states of the TPS process are identical, this product is equal to zero in centrally symmetric systems, if only the center of inversion is preserved in the excited state of the molecules. The absence of TPS spectra from the trans-form of indigoid dyes even under the strongly resonant conditions of excitation shows that this is actually so, and the adiabatic approximation for this class of compounds is well satisfied. This indicates that the symmetry of the molecules is maintained when they are adsorbed on silver particles in the hydrosol, i.e., on the validity of the principal hypothesis on the basis of which we have interpreted the results.

Perylene. Molecules of perylene, which belongs to a class of condensed compounds, differ in their high rigidity. This fact allows us to assume that in adsorption and excitation, the molecules undoubtedly preserved their inherent

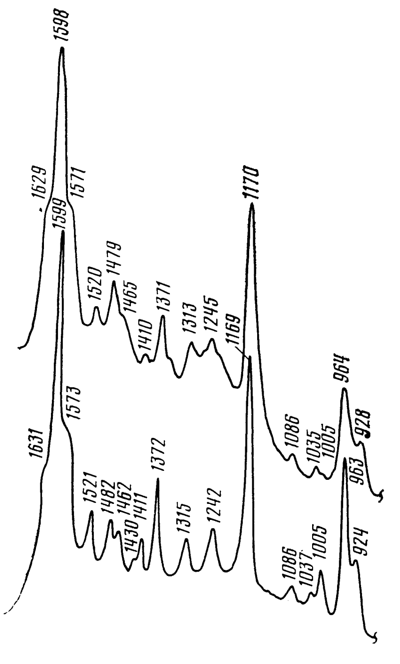
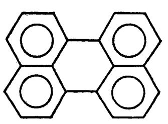


FIG. 4. Portions of the spectra of resonance TPS (upper) and Raman scattering (lower) of pyryline sol.

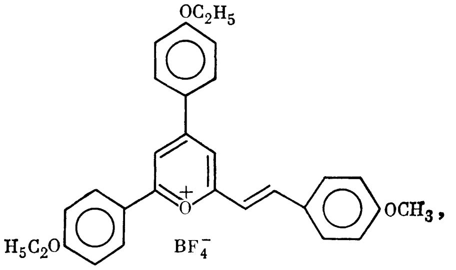
center of inversion, as is seen from the structural formula



Therefore, perylene is a very suitable object for investigation in connection with the problem of selection rules in TPS spectra.

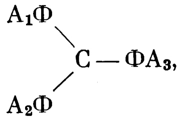
Two of us[29] earlier succeeded in obtaining very intense spectra of giant Raman scattering from perylene not only in the fundamental, but also in the overtone regions, from different wavelengths of exciting radiation, covering the range 514.5–441.6 nm. Nevertheless, attempts to obtain its TPS spectrum were unsuccessful. In our opinion, selection rules considerations suffice to explain this fact, although the reason for it in principle could also be the absence of a sharp resonance with the resolved two-photon absorption band.

Pyrilic sol. From the structural formula of the representative of this class of compounds we studied,



we conclude that its molecules are of low symmetry. It is also known that the radical with conjugated carbon-carbon bonds does not lie in the plane of the principal fragment of the molecule.[30] Either way, one should expect a close or complete similarity of the TPS and Raman scattering spectra, which is actually confirmed experimentally. We also note the high intensity and richness of lines of the spectra of this compound (Fig. 4).

Crystalline violet. This material belongs to the class of triphenylmethane dyes that have the general structural formula



where Φ is the phenyl, and A_1, A, and A are auxochromes, for crystalline violet, $A_1 = A_2 = A_3 = N(CH_3)_2$. At first glance, a rather high symmetry (D_{3h}) could be assigned to molecules of these dyes. However, in actuality, because of steric difficulties, the phenyl rings are turned somewhat about the central bond, which leads to the formation of nonplanar propeller-type (D_3) configurations or configurations lacking nontrivial symmetry elements (when two phenyl rings are turned in one direction, the third is turned in the other).[31] As a result of comparative studies of the spectra of Raman scattering and infrared absorption, the authors of Ref. 31 came to the conclusion that in solutions of crystalline violet, the configuration D_3 is realized, for which group theoretic analysis, according to Ref. 17, gives the following selection rules in vibrational spectra a_1 (Raman scattering, TPS), a_2 (infrared, TPS) and e (Raman scattering, infrared, TPS).

The complete TPS and Raman scattering resonance spectra of crystalline violet are shown in Fig. 5. As has already been noted, the latter is practically identical with the spectrum of the same material in solution without silver particles. It is seen that the spectra shown differ only in isolated details, evidently pertaining to the intensity distribution, with which the changes in the resonance conditions of exci-

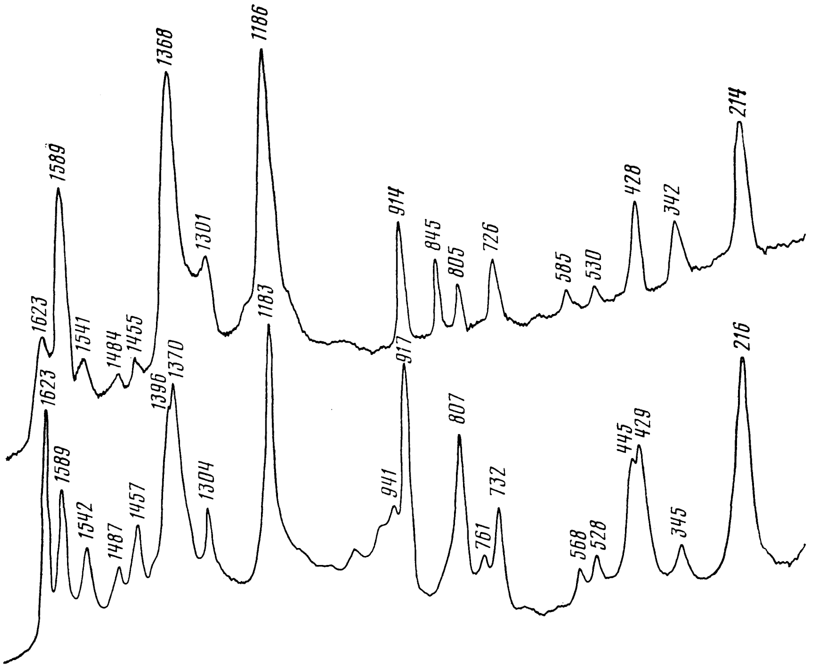


FIG. 5. Spectra of resonance TPS (upper) and Raman scattering (lower) of crystalline violet.

tation are comparable. Great interest attaches to the fact that the completely symmetrized vibrations ~ 202 and 1623 cm appear in the TPS spectrum, as should be the case according to the selection rules for group D_3 given above and provided that certain elements of symmetry in the electronically excited molecules of the adsorbate are preserved. These lines are forbidden in infrared absorption. Nevertheless, the selection rules are not satisfied in all cases. For example, in the TPS spectrum, the 445 and 941 cm^{-1} lines that are typical for Raman scattering are absent. Apparently, this can also be connected with the rules for the intensities. But comparative data on infrared absorption and Raman scattering, tabulated in Ref. 31, explicitly show the violation of the selection rules: in this and the other spectra, the observed 942 and 1171 cm^{-1} lines polarized in Raman scattering and consequently known beforehand to be related to totally symmetric vibrations. Hence for our class of dyes, the application of all three methods of vibrational spectroscopy does not give incontrovertible proof of the structure of the molecule.

In conclusion, we note that the method of giant amplification of the scattered radiation by molecules adsorbed on particles of colloidal silver, together with resonance excitation conditions and radical luminescence quenching, have allowed us, by means of the usual techniques, to obtain the spectra of inelastic TPS from a large number of dyes at very low concentration. As estimates show, all this, taken as a whole, increases the sensitivity of determination by at least eight or nine orders of magnitude. The general vibronic model of scattering assumed and established in the work turns out to be appropriate to explain a number of observed rules. By the same token, it has been shown that the combined study of the spectra of resonance TPS and Raman scattering, and also the spectra of two-photon absorption in time can be converted into a new and powerful method of analysis of the structure of the molecules.

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