

**RESONANCE STIMULATED RAMAN SCATTERING IN MOLECULAR SYSTEMS HAVING
 NORMAL AND INVERTED POPULATIONS OF ELECTRONIC STATES**

Ya. S. BOBOVICH and A. V. BORTKEVICH

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I. INTRODUCTION

RESONANCE scattering is usually taken to mean scattering in which the frequency of the light incident on an atomic or molecular system is close to one of its characteristic electronic absorption frequencies. Thereupon, the process acquires many specific features. In particular, the scattering intensity increases sharply, while its dependence on the different intermediate electronic levels becomes selective and especially distinct. These circumstances had been used long ago in the vibrational spectroscopy of spontaneous Raman scattering to study the structure of complicated molecules and the properties of their electronic states, as well as the nature and details of mechanism of the phenomenon itself.^[1] New major advances have been made along this line in recent years by virtue of the development of a very effective experimental technique, primarily involved with using semiconductor materials.

However, it is not a simple problem to obtain top-quality resonance spontaneous Raman spectra of complicated molecules. This also involves limited possibilities of interpreting the results, which hinder the development of the theory. The purely experimental difficulties are due to competing light absorption. Consequently, the optimum conditions correspond to extremely low concentrations of the substance in solution (usually 10^{-4} – 10^{-6} moles/liter), which don't always suffice to reveal all the details in the spectrum. The nature of the absorption and the specimen temperature play especially important roles. The most favorable substances for study are those having discrete absorption, especially when studied at low temperature. We shall explain the

reasons for this later. Therefore, the set of substances having known resonance spectra is still small.

It is an even incomparably harder problem to excite and interpret resonance stimulated Raman spectra. Here light absorption involves not only trivial losses, but also additional phenomena that are new in principle, and the course of the process itself depends on them very strongly. First, the absorption of powerful radiation substantially depletes the initial state. In the limit, the system becomes transparent to the incident radiation. Second, under conditions of powerful resonance excitation, triplet-triplet absorption (occurring, as a rule, in the region of the displaced Stokes lines of the spectrum) and absorption by excited singlet levels can interfere. Third, one must take into account the probabilities of stimulated absorption and emission processes closely involved in the phenomenon of stimulated Raman scattering. Fourth and last, one must take into account the effect on the molecules of the powerful radiation, which acts on them as an external high-frequency field. The latter distorts the contours and positions of the levels, as well as affecting the probabilities of transitions. This occurs especially strongly under resonance conditions. Amplification of displaced lines at exact resonance generally occurs only when there is a definite relation between the characteristics of the combining states.^[2] Special effects can also occur, but there is no need to take them up here. Besides all this, spontaneous Raman scattering also plays a large role in resonance stimulated Raman scattering. Apparently, a combination of some of the listed factors is needed to explain the fact that the experimental solution of the problem has only recently advanced to some degree.^[3]

Still, as we know, resonance stimulated Raman scattering clearly has an extremely important significance. Above all, this is because it conveys a very great volume of information on the various properties of the scattering system. Generally speaking, extraction of this information requires a complex approach to studying resonance stimulated Raman scattering and all the other concomitant processes of interaction of the powerful incident radiation with the material. The purely practical side of the problem consists in trying to use the resonance effect to lower the threshold for generation of stimulated Raman scattering, or to increase the spectral conversion coefficient of the radiation. This interesting idea has been expressed in the literature repeatedly, in particular, in the very first papers on stimulated Raman scattering.

Thus far we have tacitly assumed that the scattering system existed at the initial instant of time in the ground state, or a metastable one. However, excited atoms and molecules are just as capable of scattering light. In order to observe this phenomenon, one must create a sufficient population of the initial level, which is now an excited level. Use of powerful lasers has made it possible to solve this problem. The first results of studies involve electronic scattering in alkali-metal vapors. The initial levels were populated in these studies by using powerful Raman lasers using suitable working substances. The spectra themselves were excited by the emission line of a ruby laser.^[4-8]

The idea seemed very attractive of extending this type of study to molecular systems in order to detect scattering by the vibrational levels of their excited electronic states. In this case, the problem of populating the latter can be solved very simply. As we know, in many complicated compounds (in molecular dyes) one can rather easily even create a population inversion, and observe the concomitant generation of radiation of a rather broad spectral composition.^[9] The existence of this phenomenon led the authors of^[10-13] to think of trying to realize resonance stimulated scattering by excited molecules in a non-trivial system of quantum transitions involving an intermediate virtual electronic state located below the original and final states. For brevity, we shall call this a "downward" system of transitions. We shall show below that the Stokes scattering resonates with the luminescence under these conditions. Consequently, not only do we thus radically eliminate the usual experimental difficulties involving absorption losses, but in principle, we even make it possible to amplify the scattered radiation. This is the decisive advantage of this system of transitions, as compared with the usual one. At the same time, the ways to realize it are evident.

II. PRINCIPAL PHYSICAL HYPOTHESES AND FORMULAS

Many properties of scattered radiation are described by the Kramers-Heisenberg formula. We shall give a short resume of the results that we need which are based on this formula, following the treatment in the well-known monographic article by Placzek.^[14] Let a very simple system of particles (atoms) initially occur in a state K having the energy E_K . A light wave

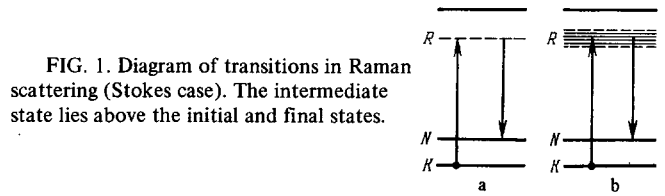


FIG. 1. Diagram of transitions in Raman scattering (Stokes case). The intermediate state lies above the initial and final states.

$E = E_0 e^{2\pi i \nu t} + E_0 e^{-2\pi i \nu t}$ is incident on it. Under its influence, the atoms scatter light. The frequency ν' of the scattered radiation is $\nu + \nu_{KN}$, where N is the final state of an atom, having the energy E_N , and $\nu_{KN} = (1/h)(E_K - E_N)$ (Fig. 1a). In order to find the scattering intensity, the problem is solved in two stages. First, one finds the eigenfunctions of the perturbed atom by the second approximation of the perturbation theory. Then, one uses them to form the matrix element of the dipole moment, and the intensity is calculated by the correspondence principle by the classical formula of Hertz. For the amplitude of this dipole moment, we get the expression

$$E_{KN} = \frac{1}{h} \sum_R \left\{ \frac{(E_0 M_{KR}) M_{RN}}{\nu_{RK} - \nu} + \frac{M_{KR} (E_0 M_{RN})}{\nu_{RN} + \nu} \right\}, \quad (1)$$

where the R are the intermediate levels, M_{KR} and M_{RN} are the matrix elements of the dipole moments, and ν_{KR} and ν_{RN} are the frequencies of the transitions that correspond to them.

Thus, the intensity (and polarization) of the scattered light is the same as that which would be radiated by a Hertz dipole having the amplitude (1), and oscillating with the frequency ν' .

After the scattering event (conversion of a quantum of frequency ν into another having the frequency ν'), the atoms go over to the state N. If $K = N$, then unshifted Rayleigh scattering takes place ($\nu_{KN} = 0$). When $K \neq N$, but $E_K = E_N$, (i.e., when electronic degeneracy exists), a special case of Raman scattering of light is realized. Finally, $K \neq N$ and $E_K \neq E_N$ corresponds to ordinary Raman scattering, which is characterized by appearance in the spectrum of lines of frequencies $\nu' = \nu \pm \nu_{KN}$ (with a sign depending on the relative positions of the levels K and N). For the sake of concreteness, we shall henceforth treat the Stokes case ($\nu' = \nu - \nu_{KN}$).

The amplitude E_{KN} expressed by (1) is a vector. However, if we consider the relation of this vector to the complex vector E_0 of the light wave, it is easy to convert (1) to the usual tensor form:

$$(\alpha_{\sigma\rho})_{KN} = \frac{1}{h} \sum_R \left\{ \frac{(M_{\sigma})_{KR} (M_{\rho})_{RN}}{\nu_{RK} - \nu} + \frac{(M_{\rho})_{KR} (M_{\sigma})_{RN}}{\nu_{RN} + \nu} \right\}; \quad (2)$$

Here σ and ρ are the symbols of the Cartesian coordinates, and the other symbols are as before.

The general selection rules for the intensity and the polarization of the scattered radiation can be derived directly by taking account of the symmetry properties of the tensor $(\alpha_{\sigma\rho})_{KN}$. We need only to keep in mind the fact that, strictly speaking, it is a complex quantity, and consequently, asymmetric as well (i.e., its non-diagonal terms depend on the order of the vibrational coordinates). Hence, it is reasonable to separate the tensor $(\alpha_{\sigma\rho})_{KN}$ into an isotropic part, a symmetric

part and an antisymmetric part. Each of them pertains to a definite form of scattering, namely, isotropic (scalar), quadrupole, and magnetic-dipole scattering.* Without writing out the corresponding expressions, we note only that magnetic-dipole scattering is forbidden when the tensor $(\alpha_{\sigma\rho})_{KN}$ is real. We shall discuss below a special case in which the selection rule is relaxed outside a resonance. The different polarization rules of the three types of scattering are also essential. For example, when the incident radiation is linearly polarized, given a suitable geometry of excitation and observation, the degree of depolarization of isotropic, quadrupole, and magnetic-dipole scattering is 0, 3/4, and ∞ , respectively. When the spectra are excited by natural light, we have the sequence of values 0, 6/7, and 2.

One of the conditions upon which the derivation of Eqs. (1) and (2) was based is that $\nu \ll \nu_{RK}, \nu_{RN}$. This excludes resonance. Indeed, an attempt to apply these formulas to the resonance case leads to infinitely large values of E_{KN} and $(\alpha_{\sigma\rho})_{KN}$, which is physically meaningless. This happens because the derivation ignored the finite duration of the intermediate state. Weisskopf^[15] has made an appropriate correction to the theory, in which the initial and final levels are metastable. He showed that, just as in the classical model of a damped oscillator, the problem is completely cleared up by adding to the denominators of Eqs. (1) and (2) a term containing a damping constant. For example, the final formula for the amplitudes acquires the form:

$$E_{KN} = \frac{1}{h} \sum_R \frac{(E_0 M_{KR}) M_{RN}}{\nu_{RK} - \nu + i\Gamma_R}, \quad (3)$$

Here the damping constant $\Gamma_R = (1/4\pi)(1/\tau_R)$ (τ_R is the lifetime of the state R). The second term in (1), whose denominator contains the sum of frequencies $\nu_{RN} + \nu$, drops out. This is because it is small under resonance conditions, and can be neglected. For clarity, the diagram of transitions in Fig. 1b shows the virtual state as a broadened level.

Now it is convenient to discuss in further detail the role of the intermediate states in scattering and the relative positions of all the interacting levels. Thus far, we have depicted the intermediate state R in Fig. 1 as being above the initial level K and the final level N, which were assumed to be metastable. This corresponds to the first term in Eqs. (1) and (2). In such a case, resonance arises when the incident radiation falls within a region of characteristic absorption of the atom.

However, one can also observe resonance with a different relative arrangement of all the levels, namely, when the intermediate state R lies below the initial and final states. Now the second term of Eqs. (1) and (2) will be responsible for resonance. The mathematical condition for such a resonance amounts to the equality $\nu = -\nu_{RN}$. However, since the incident and emitted frequencies are actually always positive, this equality can hold only when $E_R < E_K, E_N$. We see from Fig. 2 that

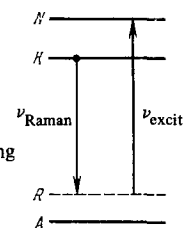


FIG. 2. Diagram of transitions in Raman scattering (Stokes case). The intermediate state lies below the initial and final states. A is the ground state.

now resonance occurs when the frequency of a Stokes line of the Raman scattering coincides with that of emission (luminescence) from the initial state.

A new circumstance is essential in scattering of light by excited atoms, in particular, of the type realized in the latter transition diagram ("downward"). This involves the necessity of taking account of the short lifetimes of the initial and final levels. The problem consists in the impossibility of fixing the positions of these levels exactly. If τ_K is the lifetime of one of them, e.g., K, then by the uncertainty principle its energy E_K is h/τ_K (or $E_K = 4\pi h\Gamma_K$, where Γ_K is the decay constant). Quite evidently, the correction in the expression for the scattering intensity must now be determined not by the decay Γ_R alone, but by some combination of all the quantities Γ_R, Γ_K , and Γ_N .

In connection with the problem being discussed (scattering by excited atoms), the method of populating the upper electronic states of the atom is also important. For example, one can excite the atom by the resonance method, using a source of powerful monochromatic radiation. However, in general, here only a certain spectral region of the broadened upper level will be populated, and thus can emit. It is also important that the properties of the source itself completely determine the phase relations of the emitted light when this method of population is used.

Nevertheless, there are ways of populating the upper states of atoms that ensure that the characteristics of the emitted light (or, in particular, scattered light) will not depend on the excitation process. An example is excitation by an incoherent continuum, which permits a uniform population of levels in the vicinity of a resonance. The problem of uniform population of levels does not arise in the systems that we are interested in, which are complicated molecules.

The physical picture and quantitative theory of light scattering by excited atoms were also developed as early as 1933 by Weisskopf.^[16] In turn, the latter theory rests on the concepts of the general theory of Dirac, which does not deal with amplitudes, but with scattering probabilities. Hence, Weisskopf treated jointly the processes of excitation of the system itself, scattering proper, and return of the system to the initial state. This required generalization of the formulas describing scattering to the case of many-quantum transitions.

Before we characterize the results obtained in^[16], let us pay attention to two physical consequences arising from the fact that the duration of the initial and final terms is short in the case of light scattering by excited particles. As before, let us depict short-lived terms by a more or less broad band having a certain density distribution (Fig. 3). Then we can easily see that this has the effect, first, of broadening the line of the scattered

*The terms "quadrupole" and "magnetic-dipole scattering" are used according to their formal similarity with the selection rules for radiation by a quadrupole and magnetic dipole.

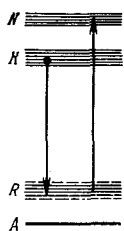


FIG. 3. Diagram of transitions in Raman scattering (Stokes case). The intermediate state lies below the initial and final states. The finite lifetime of all levels (except the ground state A) is taken into account.

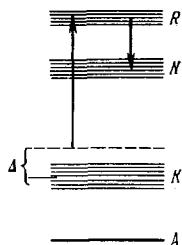


FIG. 4. Diagram of levels explaining the appearance of extra spectral lines.

radiation as compared with the exciting radiation. A less obvious effect consists in appearance of spectral lines not contained in the Kramers-Heisenberg formula. We can understand this fundamentally new effect as follows. Let scattering be excited somewhere not very far from a sharp resonance. Then, as Fig. 4 shows, the scattering intensity from the region of the broadened level K that is displaced from its center of gravity by the amount Δ may prove to be comparable with the scattering intensity arising from the center of gravity of the initial level, precisely because of the great sharpness of the resonance. This can occur in spite of the fact that the probability of finding an atom in the latter state is considerably greater. A second spectral line arises consequently.

In solving the problem of light scattering by excited particles, Weisskopf made a number of simplifying assumptions. He considered that the initial state is the ground state or a metastable state. All the calculations were made under the assumption that the density of the incident radiation $\rho(\nu)$ is small. These two simplifications eliminated the need of introducing another parameter, the decay constant of the initial (electronic) state, indeed, to the detriment of the completeness and generality of the solution of the problem. For the same reason, he assumed that the initial state is non-degenerate. He also ruled out treatment of degenerate levels K and N and other levels close to them.

By solving the posed problem with the restrictions mentioned above, he derived a general formula for the scattering probability. In particular, it describes even the anomalous scattering that appears in the additional spectral line shifted by the amount Δ from the "normal" line. The developed formulas for three possible variants of resonance are of especial interest. We shall present in final form the last of these, which corresponds to the condition $E_R < E_K, E_N$, i.e., the case of interest to us:

$$W_{KN}(\nu, \nu') = \frac{16\pi^4}{h^4} \omega_K \rho(\nu) \frac{h\nu^3}{c^3} \bar{\rho}(\nu_{KA}) \frac{\Gamma_N/\pi}{(\nu_{NR} - \nu)^2} \times \frac{\Gamma_R + \Gamma_K}{\Gamma_R} \frac{|\sum_R (M_{KR}e)(M_{RN}e)|^2}{(\Gamma_R + \Gamma_K)^2 + (\nu' - \nu_{KR})^2}; \quad (4)$$

Here ω_K is the probability that the level K will become populated upon isotropic excitation by radiation of unit

density, $\bar{\rho}(\nu_{KA})$ is the averaged density of this radiation, and e and e' are the light vectors characterizing the polarization of each radiation. If the scattering involves mainly one intermediate state R, we can omit the summation symbol. In particular, the level R can coincide with the initial level A.

As we see, in a "downward" diagram, the relation of the resonance scattering to the properties of the combining levels is rather complex, and is determined by a number of quantities, including the set of decay constants Γ_K, Γ_N , and Γ_R . The most important quantity affecting the scattering intensity is the squared sum $(\Gamma_K + \Gamma_R)^2$ in the resonance denominator that characterizes the initial and intermediate levels. This is because the second term in this denominator is small, namely, the quantity $(\nu' - \nu_{KR})^2$, which gives a measure of the sharpness of the resonance, i.e., the closeness of the scattered Stokes quantum to the emission (luminescence) from the initial state K. Among the states K and R, the one with the shorter lifetime plays the predominant role. In the limit, as $\Gamma_R \gg \Gamma_K$, the coefficient $(\Gamma_R + \Gamma_K)/\Gamma_R$ approaches unity. The physical meaning of this is that one can treat the upper electronic levels as metastable when the virtual states are very short-lived. Finally, the coefficient $(\Gamma_N/\pi)/(\nu_{RN} - \nu)^2$ characterizes the properties of the final vibrational state, and is of the order of $\sim 1/\Gamma_N$.

Let us make a crude estimate of the possible enhancement of spontaneous Raman scattering intensity owing to the resonance phenomenon. We shall compare the ordinary scattering in the region in which the material is transparent with the resonance scattering according to the discussed diagram, under the condition that the corresponding matrix elements of the dipole moments and the total population of the upper level are equal. If we assume that $\Gamma_K = \Gamma_N = 1 \text{ cm}^{-1}$, and $\Gamma_R = 10 \text{ cm}^{-1}$, we get $I_{\text{res}}/I_{\text{non-res}} = 10^6$. As will be shown below, in an actual experiment in the resonance case, the concentration of the substance being studied amounts to $10^{-4} - 10^{-6}$ moles/liter. Thus the gain in intensity fully makes up for the deficit of scattering molecules.

We have already noted that the entire theory in^[16], strictly speaking, is valid for ordinary excitation sources. If the latter are distinguished by high power, then we must first consider the finite lifetime of the initial state A. However, for complicated molecules, even when acted on by very powerful radiation, the lifetime of this state still remains substantially longer than that of the excited state. This is indicated by kinetic studies on generation of radiation by dyes and certain other independent data and considerations. Hence, we shall probably not err much if we assume that the relation of the probability W_{KN} to the various quantities given by Eq. (4) for resonance spontaneous scattering by excited molecules retains its nature in general outline, even in the presence of powerful incident radiation.

This formula is also essential in qualitative estimates of the threshold for generating stimulated Raman scattering. This is because the latter is always determined, in particular, by the spontaneous Raman scattering intensity per unit width of spectral line (in the nanosecond excitation range).^[17,18] At the same time, we can fully understand the course of the process of stimulated Raman scattering, and can estimate quanti-

tatively its threshold conditions for appearance and amplification and its coefficients of spectral radiation conversion, only with a detailed kinetic theory. There is also another very important point. Whenever the frequency of the incident radiation is close enough to one of the intrinsic frequencies of the system (resonance), it becomes very important to take account of the effect of the powerful light field on the state and properties of the scattering molecules. This effect is reflected in broadening and displacement of the vibrational levels (Stark effect), in creating inhomogeneous populations in them (saturation effect), and in altering the Einstein coefficients. Neglect of all these phenomena may prove to be too crude an approximation for solving the problem of resonance stimulated Raman scattering.

As applied to ordinary resonance stimulated Raman scattering (in an "upward" system), Ananasevich and Ordabaev^[2] have solved this problem rather fully. Platonenko has discussed special aspects of the problem in^[19]. With certain reservations, perhaps all the results obtained in these studies can be extended to the case that we are now interested in, provided we don't forget the physical meaning of the introduced quantities.

A three-level system is treated in^[2]. The state of the scattering molecules is described on the average by the so-called density matrix, whose elements satisfy a system of differential equations involving the matrix elements of interaction of the molecules with the radiation (in classical form) and the quantities d_{ik} and γ_{ik} , which are the probabilities of non-optical and optical transitions.

They assume that a biharmonic field is applied to the system. It has a frequency ω_1 (laser radiation) and a frequency ω_2 that is equal, e.g., to one of the vibrational frequencies of the molecule. In line with the generally accepted viewpoint, they assume that the second component of the field arises at the initial instant of time via spontaneous Raman scattering.

Upon making the simplifying assumptions for a steady-state system given above (and some others), the authors^[2] reduce the system of differential equations to three algebraic equations containing different combinations of quantities that have a clear physical meaning. They are the differential Einstein coefficient for the stimulated transition, the phenomenologically-introduced probability of stimulated Raman scattering (which must necessarily involve spontaneous Raman scattering), the corrections to the probabilities of stimulated transitions which are due to the joint action of both components of the field and which are associated with both broadening and displacement of the vibrational levels, the probability of finding a molecule in one of the three participating levels, and finally, the volume energy density of the field.

General estimates, and some numerical ones, are made of the characteristics of the stimulated Raman scattering in two cases.

The first of these is quasiresonance scattering, which is characterized by the inequalities $|\omega_{31} - \omega_1| \gg \gamma_{31}$ and $|\omega_{31} - \omega_1| \ll \omega_2$ (Fig. 5). With a frequency mismatch provisionally set at $100 \gamma_{31}$, and with typical values of all the other quantities, it becomes essential to account for the displacement and broadening of the vibrational levels at excitation powers of the order of

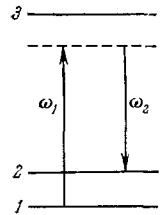


FIG. 5. Diagram of levels explaining the analysis of the stimulated Raman scattering process in^[2].

10 and 1000 gigawatt, respectively. The shift in the vibrational levels leads to an adequate shift in the stimulated Raman line without appreciably affecting its power. Conversely, broadening of the vibrational levels can considerably alter the transition probabilities, and hence also the stimulated Raman scattering power. Further, it turns out that the threshold value of the field component of frequency ω_1 (i.e., the minimum value E_1 of this quantity at which the field E_2 is amplified) is insensitive to resonance under the discussed conditions.

This latter conclusion has been subjected to criticism and refinement in^[19], where it was shown that this situation results from neglect of the non-resonance fraction of the linear losses in the medium. This is permissible only when the second level is appreciably populated. However, if the population is small (as may occur, e.g., in the absence of appreciable saturation and in scattering of large vibrational quanta), then the threshold for generation of stimulated Raman scattering proves to be proportional to $(\omega_{31} - \omega_1)^2$ over a broad spectral range of excitation conditions. Hence, resonance stimulated Raman scattering should be an especially effective means of studying lines having large vibrational frequencies.

The second case for which stimulated Raman scattering is treated in^[2] is a sharp resonance in which the frequency ω_1 of the incident radiation and ω_2 of the scattered radiation differ from intrinsic frequencies of the molecule only by amounts of the order of γ_{31} and γ_{32} , respectively. Here the effect of the radiation on the state and properties of the molecules increase extremely rapidly. The conditions under which the radiation of frequency ω_2 can be amplified become very strict. In particular, amplification will always be observed only in special cases in which the half-width of the Raman line exactly coincides with the reciprocal of the lifetime d_{21} of a molecule in level 2, or when the lifetime of level 2 is less than that of level 3. Apparently the latter happens extremely rarely.

The study of Platonenko^[19] contains very useful estimates, that permit comparison with experiment as well. He considers a transition from quasiresonance to exact resonance, and distinguishes as before the cases of large and small non-resonance losses. Apart from neglect of the contribution of other intermediate states to the non-resonance scattering, the maximum decrease in the generation threshold K (as defined by the ratio $|E_1|_{\text{threshold}}^2 \text{non-res} / |E_1|_{\text{threshold}}^2 \text{res}$) for typical molecular characteristics can attain many orders of magnitude ($10^5 - 10^6$), according to^[19]. At the same time, when the resonance linear losses predominate, decrease in the generation threshold is generally problematical, while in any case its amount must be less.

The theoretical analysis conducted in the same study^[19] of the conditions for the effect of various factors on the population of levels 2 and 3 is also worthy of much attention. In particular, it is very important to take into account the non-equilibrium population of level 2 arising from the Raman scattering process itself. Since this phenomenon can be easily simulated by using an auxiliary source of powerful non-resonance radiation, i.e., by subjecting the system simultaneously to two radiations of different frequencies, the conclusions of the theory can be subjected to test. This problem will be taken up in the presentation of the experimental material.

A very essential fact in studying resonance stimulated Raman scattering of molecular systems, and one that has been overlooked insofar as we know, is that they very probably show triplet-triplet absorption. The nub of the problem consists in the idea that these transitions fall in the spectral region where the Stokes lines of the stimulated Raman scattering lie, while a sufficient population of the lower triplet state becomes quite attainable under powerful (even pulsed) excitation. In this situation in a quasiresonance case, the triplet-triplet absorption losses can dominate over the singlet-singlet absorption losses, and seriously interfere with amplification of stimulated Raman scattering. At the same time, the phenomenon that we are discussing (triplet-triplet absorption) opens up an attractive perspective for studying resonance spontaneous and stimulated Raman spectra belonging to the lower triplet state, and which hence characterize the vibrational transitions in this distinctive electronic state.

Thus we see from even a cursory review of the literature that the problem of obtaining and interpreting resonance stimulated Raman spectra is extremely complex. However, the volume of scientific information contained in the phenomenon that can be got from the spectra more than pays for the difficulty of solving it. Hence, studies along this line are very important and timely.

In closing this section, we shall make one remark on a specific feature of Raman scattering by excited molecules.

Earlier we paid special attention to the fact that the scattering tensor $(\alpha_{\sigma\rho})_{KN}$ is a complex quantity in the general case. We had in mind resonance scattering by atoms or molecules in their ground or excited states, but imposed no restrictions on the concrete system of quantum transitions. Placzek^[14] has discussed this problem in part. For example, he took into account the fact that the complex nature of the tensor $(\alpha_{\sigma\rho})_{KN}$ under resonance conditions increases the degree of depolarization of spectral lines. This involves the appearance of magnetic dipole scattering, which is forbidden outside resonance. Perhaps it is just this reason that explains the results of studying the polarization relations in spontaneous Raman spectra excited within an absorption band, e.g., for carbon disulfide in^[20].

Another cause of complications of the same type is specific for complex, non-linear molecules, and here it is substantial in practice, precisely in the case of scattering from excited levels. We are speaking of electronic degeneracy, which is eliminated by certain antisymmetric vibrations. Let us take up this problem in somewhat more detail.^[21,22]

For example, let a non-linear molecule be in a doubly-degenerate electronic state. We shall take into account the electronic-vibrational interaction ($\psi_{\text{total}} \neq \psi_{\text{el}}\psi_{\text{vibr}}$). The Jahn-Teller theorem states that such a system has at least one antisymmetric coordinate that gives rise to a splitting of the potential function such that its minima do not correspond to a symmetric position, but are separated evermore with increasing electronic-vibrational interaction. In other words, unstable configurations arise in such vibrations (Fig. 6). A consequence of this can be a change in the symmetry of the electronic wave functions, with concomitant appearance of a magnetic-dipole component of the scattering.

We know of only one study^[23] which has treated theoretically, among other problems, Raman scattering of light by a hypothetical triangular plane molecule under equilibrium conditions according to Jahn-Teller. The authors showed by direct calculation that the degree of depolarization of certain lines in the spontaneous Raman spectrum can actually be very large, owing to breakdown of the selection rule against magnetic-dipole scattering. This is especially true when the scattering is excited by linearly polarized light. Unusually intense overtones can be exhibited. The lines of both these overtones and the fundamental Jahn-Teller vibrations are split into a number of components corresponding to the initial degree of degeneracy of the electronic state. When the electronic-vibrational interaction is very strong, the observed Raman spectrum is better interpreted as pertaining to ordinary scattering, but for a less symmetrical molecule. The latter is also characteristic of the infrared spectra of such molecules.^[24] All that we have noted above can also be manifested in stimulated Raman spectra. As for the polarization relations, they are manifested at least in the vicinity of the threshold for generation of spectra.

However, while cases of a degenerate electronic ground state are quite exceptional, they are typical in scattering by excited molecules. The general theory of this scattering is markedly complicated thereby. Moreover, its semiclassical variant based on the adiabatic approximation (with nuclei moving much more slowly than the electrons), which permits one to separate the vibrational from the electronic eigenfunction, becomes no longer applicable ($\psi_{\text{total}} \neq \psi_{\text{el}}\psi_{\text{vibr}}$). Hence, experimental solution of the problem of obtaining Raman spectra corresponding to vibrational transitions in excited electronic states of molecules poses a very serious problem to the theoretician.

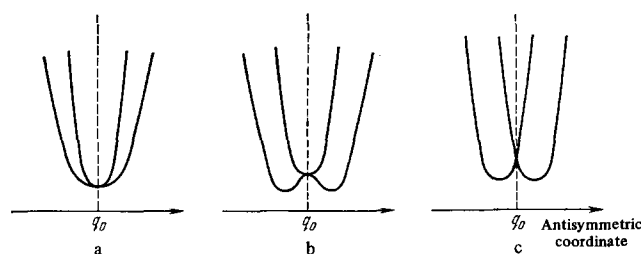


FIG. 6. Different cases of electronic-vibrational interaction: a) A linear molecule, with weak interaction; b) the same, with strong interaction; c) a non-linear molecule, with strong interaction. In the latter case, q_0 does not correspond to the minimum in potential energy, i.e., non-equilibrium configurations arise.

III. REQUIREMENTS IMPOSED ON THE SUBSTANCES BEING STUDIED. PROCESSES ACCOMPANYING RESONANCE STIMULATED RAMAN SCATTERING. EXPERIMENTAL SYSTEMS

First, let us examine the conditions for obtaining stimulated Raman spectra within and near intrinsic absorption bands, i.e., by unexcited molecules.

We see from Eq. (3) that the resonance enhancement of scattering lines is determined here by the decay constant of the intermediate (virtual) level. The greater the lifetime of this level is, the sharper the resonance effect. Hence, the most suitable substances for study are those having discrete electronic absorption spectra, i.e., with an (at least partially) resolved vibrational structure. This circumstance has been confirmed experimentally by Shorygin and his associates with the example of resonance spontaneous Raman spectra of polyene compounds.^[25,26] According to the estimate of^[25], the lifetime of the virtual states for liquid solutions of the cited substances is of the order of 10^{-11} – 10^{-12} sec. We can expect a further increase in lifetime upon crystallizing the substance at low temperature. Moreover, under these conditions the spontaneous Raman cross-section is very large at the peak of the line, while the absorption is characterized by a steep front on the long-wavelength side. All of this creates a favorable situation for amplification of the scattered radiation.

However, it is not always expedient to proceed too far in increasing the lifetime of the intermediate state. A limit is imposed by the condition of a steady-state process. That is, to use classical terminology, it is imposed by the question of whether it is valid to separate the stimulated and intrinsic vibrations of the electronic oscillator. As applied to spontaneous resonance emission from the ground state, this problem has been discussed in detail by Shorygin and Krushinskiĭ.^[27,28] They distinguish several cases, corresponding to the relation between the quantities Γ_{el} , Γ_{exc} , and ω_{vibr} (the widths of the electronic absorption band and the line of exciting light and of the vibrational frequency). When $\Gamma_{el} \gg \omega_{vibr} > \Gamma_{exc}$, we can have resonance Raman scattering that is distinguished from non-resonance scattering mainly by the sharp enhancement of intensity of the spectrum. The nature of the intensity distribution over the spectrum remains typical for the scattering. The position and contour of the displaced lines depends on the analogous parameters of the exciting light. The fraction of delayed emission in the secondary radiation is very small. If $\omega_{vibr} > \Gamma_{el} > \Gamma_{exc}$ (which is expressed in the appearance of vibrational structure in the absorption band), the secondary-emission spectrum acquires certain features of luminescence. In particular, it becomes widened because of the anomalous intensity of overtones of different orders that approximately coincide in position with the vibrational maxima. The authors^[27,28] associate these spectra with Type I transition phenomena. They have been observed in^[29,26]. As Γ_{el} decreases further ($\omega_{vibr} > \Gamma_{el} \cong \Gamma_{exc}$), luminescence features begin to dominate in the secondary resonance emission spectrum: each spectral line approximately reproduces the contour of the intrinsic lines of the oscillator, the dependence of the position of

the spectrum on the frequency of the exciting light becomes weaker or totally vanishes, and the fraction of delayed emission becomes large. We could say that the secondary-emission spectrum "forgets" its excitation conditions. In the terminology adopted in^[27,28], this corresponds to Type II transition phenomena. Resonance luminescence and spontaneous Raman scattering can also coexist (see, e.g.^[17]).

Thus, it was shown in^[27,28] that the assignment of resonance secondary emission as being scattering or luminescence is determined to a considerable degree by the properties of the system being studied and by the experimental conditions.

As we have noted, the lower triplet level can become rather well populated when stimulated Raman spectra are excited in an absorption band, owing to intramolecular energy transfer. Hence, in the general case we have to deal with triplet-triplet absorption, which is usually shifted toward longer wavelengths than the singlet-singlet absorption. This same region contains the Stokes lines of typical frequencies in the stimulated Raman scattering.

The accumulation of molecules in the triplet state is governed by the spectral position of the absorption, the relaxation times of all the transitions, and hence, also the physical state of the substance, and the duration and power of the pulse. The conditions for this process are especially favorable in rigid matrices and at low temperatures. Therefore, the losses due to triplet-triplet absorption are quite substantial. Figure 7, which is taken from^[30], shows the relative positions of singlet-singlet and triplet-triplet absorption spectra.

The transition of molecules from the original electronic state, e.g., to the triplet state is harmful per se, and this is because this process competes with the stimulated Raman scattering. If, in addition, laser action begins under corresponding conditions, then it can completely suppress the Raman scattering by unexcited molecules by virtue of the fact that its threshold lies considerably lower, as a rule. The attenuation of the pulse expended in exciting transitions that compete with stimulated Raman scattering is also substantial.

Another interference involves a probable absorption in the singlet channel due to transitions from the first excited level to the next higher one. This process can

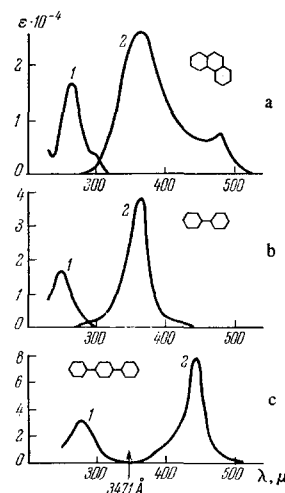


FIG. 7. Spectra of singlet-singlet (1) and triplet-triplet (2) absorption of liquid solutions of some substances, according to the data of [6], a) 9, 10-dihydrophenanthrene; b) bibphenyl; c) p-terphenyl.

play a role when the initial state is well enough populated. If inversion is attained and laser action starts, then this type of absorption is sometimes appreciable, and is actually observed from indirect manifestations. The pertinent facts will be treated in discussing the problem of behavior of dyes.

It would seem that a radical way out of the situation would be to use the systems of Shpol'skiĭ to study stimulated Raman scattering. As early as 1952, Shpol'skiĭ and his associates showed that substances crystallized at low concentrations (10^{-3} – 10^{-7} moles/liter) in neutral solvents such as the normal hydrocarbons show discrete absorption and emission spectra^[31,32] at low temperatures. This remarkable effect, which has subsequently been called in the literature the Shpol'skiĭ effect, has become the topic of many studies, and has been made into a unique method for getting information on vibrational transitions in the excited electronic states of molecules.^[32,33] Thus, the idea consists in choosing Shpol'skiĭ systems for which the exciting line falls in an interval between absorption lines. Of course, such systems can prove to be promising only under the condition $\Gamma_{el} > \Gamma_{exc}$ (see above). An independent, interesting problem here is pulse excitation of quasilinear emission spectra in the case in which the exciting line is close to an absorption line.

If we take into account all that we have said above, we must consider the most suitable objects for studying resonance and quiresonance stimulated Raman scattering by unexcited molecules to be the aromatic condensed compounds. As a rule, they absorb in the near ultraviolet. This then determines the excitation source. This is the ruby-laser harmonic ($\lambda = 3471 \text{ \AA}$).*

The basis of the method for exciting quiresonance spectra in^[3,36] is the phenomenon of generation of stimulated Raman scattering in polycrystalline materials that was discovered by Sushchinskiĭ and his associates.^[37] A liquid frozen into a polycrystalline state or a fine powder was irradiated by a focused beam of radiation of the ruby-laser harmonic having a power of 1–3 megawatts.

The spectra were photographed with an ISP-66 quartz spectrograph on Pankrom-10 film. An STĖ-1 spectrograph was used in individual cases. Observation was made in reflected light at an arbitrary angle. The substances (stilbene, tolan, naphthalene, benzene, toluene, etc.) as well as the corresponding matrices were cooled to 77° K.

Two conditions must be satisfied in order to observe resonance stimulated Raman scattering by excited molecules in a "downward" system of transitions. First, one must create an inverted population, and hence, laser action must arise (stimulated luminescence), with which the stimulated Raman scattering resonates. Second, it must be certain that the upper electronic state is discrete. Inverted population is easily attained in dyes, which are the most suitable

substances for such studies.^[9] Until recently, the situation was less definite concerning the second question (the discrete structure of the absorption bands), at least in liquid solutions. The relative durations of the upper and lower states are also essential. Along this line, we shall briefly summarize the fundamental experimental facts and results from study of the laser-action properties of dyes, without at all pretending to encompass the literature fully nor to treat exhaustively this large and independent problem.

In order to understand deeply all the processes that occur in dyes when irradiated with a powerful light pulse, one must generally examine a rather complex diagram of levels. It is given in Fig. 8. The left-hand part of the diagram pertains to the singlet channel, and the right-hand part to the triplet channel. As usual, the solid arrows indicate optical transitions, and the wavy arrows characterize pathways of non-optical energy conversion. The corresponding relaxation times are denoted by τ_{ij} . However, many properties of laser action can be understood even on the basis of the simplest model consisting of two broadened levels. Stepanov and Rubinov^[9] have conducted an rounded theoretical analysis of such a model. Here they did not even take into account in explicit form the relaxation characteristics of each of the broadened levels. They established requirements on the properties of the working substance. In particular, they showed that optimum conditions for laser action are attained (with maximum probability of the corresponding spontaneous transition) in compounds whose absorption and emission spectra have the broadest bands. Using the theory that they had developed, they were able to explain (and predict) a number of facts, e.g., the behavior of the amplification coefficient as a function of the frequency and spectral composition of the incident radiation, the concentration and temperature of the substance in the solution, the relative arrangement and shape of the absorption and luminescence bands, the parameters of the resonator, etc. They calculated the threshold and power of laser action.

A number of facts that were already known at the time that Stepanov and Rubinov wrote their review, as well as some established later, however, do not fit into

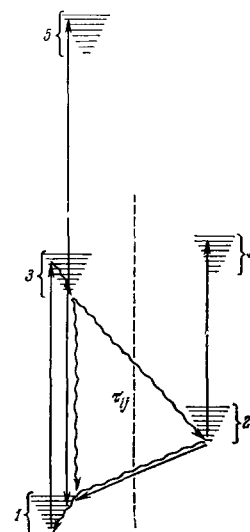


FIG. 8. Overall diagram of levels explaining the process of laser action in dyes. The left-hand side involves the singlet channel, and the right-hand side the triplet channel.

* According to the data of a number of measurements (see e.g. [34, 35]), the width of the 6943-Å emission line of a ruby laser operating in a giant-pulse mode (with Q-switching with a passive shutter) lies in the range 0.01–0.02 cm^{-1} . The spectral width of the harmonic is even smaller.

the idealized scheme discussed above, and some questions are raised that are of importance in principle.

Perhaps the most interesting of them involves the problem of the so-called "hole burning" in the absorption band of a number of dyes. That is, they are locally bleached. Apparently, this effect was first observed by Roess with the example of the dye Sudan Black B excited by a ruby laser.^[38] Soffer and McFarland^[39] have obtained an analogous result, and also Spaeth and Bortfeld^[40] for free phthalocyanine and polymethine dyes, respectively. However, it had been previously shown in the experiments of Gires and Compaud,^[41] Kosonocky, Harrison, and Stander,^[42] and also Armstrong^[43] that free and metal-substituted phthalocyanines are bleached throughout their bands. The special position of dyes of the latter type was confirmed by Spaeth and Sooy.^[44] This problem has subsequently been the subject of a further series of studies that have firmly established the fact that there are two types of dyes: those that saturate locally, and those that saturate mainly throughout the band.^[45,46,47] At the same time, by varying the spectral width of the giant pulse and measuring the transmission as a function of its power and by another method, it has been shown that the lower limit of the width of the "burnt-through hole" amounts to less than 1 cm^{-1} .^[47,48]

A natural possibility of interpreting the facts described above consists in assuming that local bleaching occurs within a broadened, but nevertheless discrete, vibrational level of the upper state. In other words, the upper electronic state is viewed here as being inhomogeneously broadened. Here its inhomogeneous broadening has been ascribed to differing absorption centers, i.e., to a discrete set of molecules that absorb light under conditions of varying environment that determines the force field. An example of this is the theoretical study.^[49]

Soffer and McFarland^[39] also initially came to an analogous conclusion. However, after their successful experiments on the narrowing of the laser-action band of a dye by introducing a diffraction grating into the resonator as a mirror, they had to reject their viewpoint, and to assume that the absorption band is primarily broadened homogeneously.^[50]

Bass and Deutsch^[51] are inclined to view the results of their study on amplification of stimulated Raman scattering harmonics of toluene and carbon disulfide in solutions of polymethine dyes as another argument against the assumption that the upper state is inhomogeneously broadened. It turned out that the amplification of the lines is accompanied by marked weakening of the entire laser band. In the opinion of the authors,^[51] such a broad-band amplification is direct evidence of very fast relaxation in the system of sublevels of the upper state, i.e., of homogeneous broadening of the absorption band. Derkacheva and Sokolovskaya^[52] have subsequently made analogous observations. However, we note that no substantial weakening of the laser-action band during the amplification process was noted in independently conducted experiments on amplification of stimulated Raman lines.^[53]

A very important advance has been to study the kinetics of laser action by dyes. Unfortunately, only three studies along this line are known in the literature.

In one of these, which was conducted by Gibbs and Kellock,^[54] the kinetics of development of the laser-action band was followed in solutions of cryptocyanine and chloroaluminum phthalocyanine. In the former case, they stated that the band shifted with time toward longer wavelengths. The time development of the band has a discrete structure. There were no such effects in the latter case.

In our opinion, the results for cryptocyanine are interpreted without enough justification as evidence for inhomogeneous broadening of the lower state alone.

Bass and Steinfeld^[55] have also shown a distinct course of development of emission with time. Here they noted that short wavelengths reach their emission peak earlier than longer ones. They see a reason for this in induced absorption. They also emphasize that a large Stokes shift favors laser action. Therefore, the phthalocyanine dyes generate poorly or not at all. If the absorption and luminescence bands almost coincide, then laser action does not arise because the system degenerates into a two-level system that does not give rise to inversion. In the semiclassical approximation, such systems should give only weak Raman spectra. Following the generally-accepted view, the authors of^[55] assume that relaxation of the excess vibrational energy in the excited electronic state occurs in a time no greater than 10^{-10} – 10^{-11} sec for large molecules in liquid solutions. Conversely, on the basis of their own work and the results of studies by other methods, the lifetime of the vibrational levels for the lower electronic state is assumed to be considerably greater. Limits of 10^{-6} – 10^{-8} sec are adopted for it. The pattern is probably the same in rigid (in particular, in crystalline) systems at low temperature (as regards relative estimates). It is natural only to expect that in this case the upper state as well is inhomogeneously broadened. This is indicated by the fact that certain single crystals at low temperature show discrete spectra.

Finally, the last of the kinetic studies, which was conducted by Farmer, Huth, Taylor, and Kagan,^[56] showed that the laser-action band shifted systematically with time toward longer wavelengths in a solution of a polymethine dye. At each interval of time, the band shows a structure with two peaks at the edges. At a certain concentration of the substance, the time course of the laser-action band ceases to vary monotonically. A maximum spectral shift is attained (about in the middle of the pulse), and then the shift reverses. This time behavior of the band involves inclusion of triplet-triplet absorption in the process. No detailing of the role of the latter is given.

As we have emphasized above, the phenomenon of "hole-burning" in the absorption band of dyes is of great significance with regard to the problem of the nature of broadening of levels, and hence, of their corresponding lifetimes. This side of the question defines the perspectives of getting stimulated Raman spectra in a "downward" system of transitions, as well as the approach per se to interpreting them. It is no less important to know how great the remaining absorption in the frequency region of the incident radiation is, and what it arises from (i.e., how deep this "hole" is), and to elucidate the conditions for bleaching of dyes throughout their absorption band.

The cited problems have been the topic of thorough studies by Hercher, Chu, and Stockman,^[57] who have given a critical review of all the pertinent material and supplemented it with their own results on frequency selection in experiments with two lasers, and they analyzed the processes of laser action by means of kinetic equations. They concluded that the broad absorption band breaks down during pumping into a series of spectral regions. For chloroaluminum phthalocyanine dissolved in pyridine, the relaxation time for this process is 5×10^{-12} sec. The remaining losses in this material are large, and are mainly due to singlet-singlet transitions from the excited levels. Hence, dyes of this type work poorly as Q-switching agents at high powers (above ~ 10 megawatts/cm²). Perhaps the varying behavior of these dyes as a function of the excitation power is the reason for the apparent contradiction in the literature data. Conversely, cryptocyanine, and apparently the other polymethine dyes, strongly possess the property of local bleaching with small residual losses under conditions of powerful excitation. Its probable nature is twofold. In particular, it involves depletion of the inhomogeneously broadened ground state over a spectral range of 1–60 cm⁻¹. Thus, according to the signs of a large Stokes shift and smaller residual losses, the polymethine dyes merit unconditional preference as objects for studying resonance stimulated Raman scattering in the excited state.

A rounded discussion of the entire complex of problems of interest to us is found in one of the recent studies conducted by Weber and Bass^[58] on laser action in dyes, together with a presentation of new experimental data. They studied rhodamine B and 6G, 7-hydroxycoumarin, and anthracene. The substances were chosen on the principle of features of their absorption and emission spectra, in particular, the size of the Stokes shift. The experimental method consisted in studying the kinetics of laser action with a time delay produced by a Pockels cell. The results were treated theoretically by setting up and solving (by computer) the kinetic equations under varying initial conditions. They showed for rhodamine 6G that a very simple diagram agrees with experiment, and that the instant of opening the gate affects the width of the laser-action band. The latter relation was lacking in 7-hydroxycoumarin. Then they estimated the time constants of the relaxation processes. With the example of rhodamine B and anthracene, they demonstrated the role of triplet-triplet absorption losses. Thus they showed that such losses are quite substantial in individual cases, and one must take them into account.

Thus, the results of varied studies of laser-action characteristics, as well as those of features of absorption and luminescence of dyes in liquid solutions and certain side effects are compatible with a model in which the upper state is assumed to be preferentially homogeneously broadened, while the lower state is inhomogeneously broadened. In any case, they show that the lifetimes of the vibrational levels of the ground state must be considerably longer than those of the excited state. It is very likely that the latter conclusion still holds in rigid systems at low temperature. As for the nature of the broadening of the absorption bands in such systems, there are experimental data that directly show

the existence of vibrational structure of the bands in various dyes, and in particular, the polymethine dyes.^[59]

Thus, some promising substances for studying resonance stimulated Raman scattering by excited molecules are the polymethine dyes (and in particular, cryptocyanine) frozen at low concentration in glassy or (preferably) crystalline matrices. An almost total inversion can be created and laser action excited easily in such systems with a ruby-laser giant pulse. If the Stokes shift is not very large, it can serve for excitation of resonance stimulated Raman scattering itself, at least at large vibrational frequencies. This can be seen from Fig. 9. In the general case it is more convenient to use an auxiliary radiation source of somewhat lower frequency. In principle, a Raman laser is suitable.

IV. QUASIRESONANCE STIMULATED RAMAN SPECTRA OF UNEXCITED MOLECULES

Study of this problem is complicated by the concurrent effect of another factor besides the resonance factor on the threshold and intensity of stimulated Raman scattering. This involves change in frequency of the exciting light. The point is that the intensity of Raman scattering is proportional to the quantity $(\nu \pm \nu_{\text{vibr}})^4$, where ν_{vibr} is the frequency of a vibrational line, and the lower sign corresponds to the Stokes case of scattering.

The only study that we know which makes possible an estimate of the contribution of the frequency factor to stimulated Raman scattering is that of Khokhlov, Akhmanov, and their associates.^[60] They excited stimulated Raman spectra in liquid benzene and cyclohexane with focused beams of the fundamental radiation of a ruby laser ($\lambda = 6943 \text{ \AA}$) and the harmonic of a neodymium laser ($\lambda = 5328 \text{ \AA}$). Here it turned out that the stimulated Raman scattering threshold in the latter experiments was lower by a factor of about two, e.g., for benzene.

On the basis of the factor $(\nu - \nu_{\text{vibr}})^4$ alone, one should expect an almost threefold decrease in the threshold for laser action. On the other hand, the authors of^[60] did not take into account the smaller divergence of the light beam of the neodymium laser harmonic, as compared with the ruby laser. Therefore, the true picture of disagreement of expected and obtained results is even more striking. Furthermore, the resonance effect should also make a certain (however small) contribution to the measured quantities. Indeed, they didn't take into account in^[62] the fact that the Q-switching with a rotating prism which was used in the neodymium laser gives a laser line of large width.

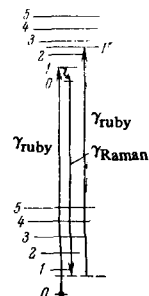


FIG. 9. Diagram of pumping and excitation of stimulated Raman scattering by vibrational transitions of the upper electronic state, using a ruby laser. The case is treated of a small Stokes shift and large vibrational frequencies.

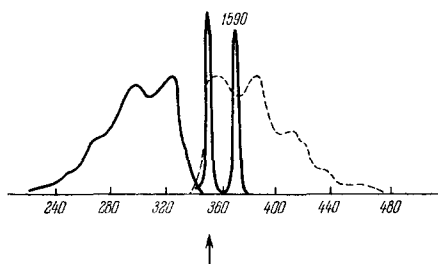


FIG. 10. Absorption (solid line), luminescence (dotted line) and stimulated Raman spectra of stilbene. The arrow indicates the exciting line at 3471\AA . The number is the vibrational frequency of the stimulated Raman line in reciprocal centimeters.

Its harmonic is also consequently broadened. To some extent, this can compensate the effect of its smaller divergence.

While considering all the reservations that we have made, we can still consider it established that in the Placzek region the law of variation of the intensity of stimulated Raman scattering as a function of the frequency is much less sharp than $(\nu \pm \nu_{\text{vibr}})^4$.

The authors of^[13] were able to approach considerably closer to the absorption band in a study of stimulated Raman scattering. This can be illustrated by the stimulated Raman spectrum of finely crystalline stilbene. This is shown in Fig. 10 in schematic form, along with the absorption and luminescence spectra. In this case, the distance of the exciting line ($\lambda = 3471\text{\AA}$) from the first vibrational peak of the discrete absorption band amounts to only 2000 cm^{-1} . The luminescence spectrum shown in Fig. 10 belongs to the substance itself, rather than any impurity. Shorygin and his associates^[25,26] had previously observed coexistence of luminescence and spontaneous Raman scattering. The 1590-cm^{-1} line excited in stimulated Raman scattering belongs to an antisymmetric vibration of the benzene rings. One cannot measure the exact values of the laser-action thresholds, and it is difficult to compare them with the corresponding quantities in the case when the fundamental radiation of a laser is used for excitation. This is because the variations in experimental conditions do not lend themselves to being accounted for. Nevertheless, they are evidently much larger than one would expect from taking into account the spontaneous Raman scattering cross-section alone. Indeed, an estimate by the well-known formula of the semiclassical theory shows that the spontaneous Raman scattering cross-section for stilbene should be increased by a factor of no less than 10^4 by the resonance effect. Hence, there are processes that interfere with resonance stimulated Raman scattering, and the law $I(\nu - \nu_{\text{vibr}})^4$ is not obeyed.

In the same study, as well as^[36], they studied the spectra of other aromatic condensed systems: tolan and naphthalene. These substances begin to absorb appreciably at shorter wavelengths than stilbene. Hence, they are practically transparent to the incident radiation. This is probably related to the relatively high intensity of their stimulated Raman scattering lines (2225 and 1380 cm^{-1} , respectively). Increasing the excitation power (to 3 megawatts) leads to the appearance in the spectrum of naphthalene of two harmonics of the funda-

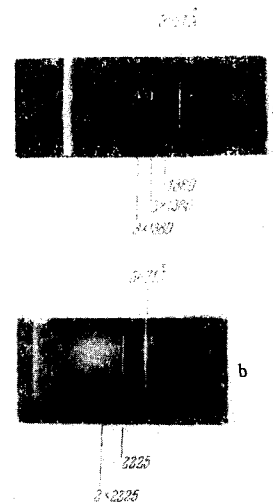


FIG. 11. Stimulated Raman spectra of naphthalene (a) and tolan (b) at 77°K .

mental line, and of one weak harmonic in that of tolan. This can be seen in Fig. 11.

Other objects for which the effect of approach of the frequency of the exciting light to the intrinsic-absorption region has been studied have been crystallized liquids: benzene, toluene, styrene, and chlorobenzene. The first three substances have the feature that their stimulated Raman spectra each contain two or three lines. In particular, in the benzene spectrum, vibrations of the C—H bonds are excited as well as the totally symmetric skeletal vibrations. However, indeed, the former appear as a weaker line (the pattern is the opposite in toluene). It is hard to understand this result by taking into account only the properties of the spontaneous Raman scattering of the same substances. This is because the absorption bands involving vibrations of the C—H bonds lie at shorter wavelengths than those of the skeletal vibrations. We shall try below to interpret this phenomenon.

In connection with the latter observations, an additional study was made in^[36] of certain saturated hydrocarbons and acetone, in which the vibrations of the C—H bonds could be excited under conditions avoiding competition of the skeletal vibrations. In all cases (hexane, heptane, nonane, octane, and acetone), the stimulated Raman spectra showed the lines of the stated vibrations.

The stimulated Raman spectrum of carbon disulfide could not be excited in^[3,36] in either the pure, frozen substance, nor in glassy matrices containing various concentrations of it (down to a minimum of 3×10^{-2} moles/liter). In this case, the exciting line falls near a weak intrinsic absorption band ($\lambda_{\text{max}} = 3200\text{\AA}$, $\epsilon_{\text{max}} = 70$). The extinction coefficient of the 3471-\AA line amounts to only 4 (while being ~ 12 for stilbene). The negative result seems strange, since carbon disulfide, as we know, is distinguished by the lowest threshold for generating stimulated Raman scattering among all substances thus far studied when irradiated outside the absorption region, and its resonance spontaneous Raman spectrum is rather easily excited.^[20]

Attempts to excite with the laser harmonic the stimulated Raman spectra of a number of other compounds also failed (bromoform, o-dichlorobenzene, p-dibromobenzene, biphenyl, bromobiphenyl,

4, 4'-dibromobiphenyl, bromodimethylaniline, quinoline, anthracene, and diphenylbutadiene). In the latter case the matrix method was used, and the concentration of the substance was reduced to 10^{-2} moles/liter.

As has been noted, one of the reasons for difficulty in exciting stimulated Raman scattering, although far from being the only one, involves absorption losses. This concerns absorption in the singlet and triplet channels in the diagram of Fig. 8. Hence, an attempt was undertaken in^[36] to extend the studies to a Shpol'skiĭ system.*

However, negative results were obtained in^[36] even in studying Shpol'skiĭ systems: stimulated Raman spectra could not be excited in the region of quasilinear absorption in even a single case. Nevertheless, the Shpol'skiĭ discrete emission spectra per se of the series of substances were obtained without difficulty when excited by the 3471-Å line. Figure 12 gives some examples of this. Use in these experiments of a high-dispersion spectroscopic instrument showed that the width of the lines in the Shpol'skiĭ emission spectra is of the order of about 20–25 cm^{-1} under pulsed excitation. These values exceed those typical of these spectra when excited by a source of relatively low-power continuous radiation. This can be caused by the somewhat higher local temperature of the specimen at the focus of the incident light pulse.

The question arises of to what one should ascribe the Shpol'skiĭ spectra obtained in^[36], namely, to stimulated or spontaneous processes. Apparently we cannot yet provide a definite answer. However, the results of a recent study by Kohlmannsperger^[61] make it possible to ascribe these spectra preferentially to stimulated scattering. The basis of this is the fact that their gen-

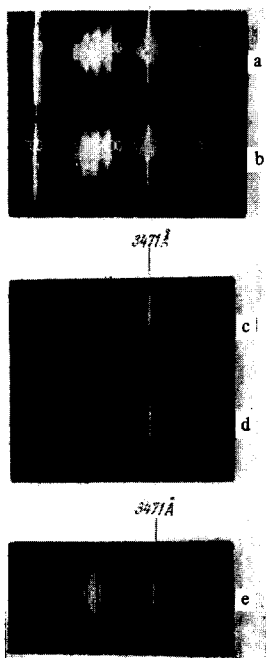


FIG. 12. Spectra of solutions of 9-methylanthracene ($C = 10^{-5}$ moles/liter) in hexane (a) and acetone (b); of perylene ($C = 10^{-5}$ moles/liter) in hexane (c) and acetone (d); and of coronene ($C = 10^{-5}$ moles/liter) in heptane (e).

*The width of the components of Shpol'skiĭ quasilinear absorption spectra amounts to no less than several reciprocal centimeters. Hence, the condition $\Gamma_{el} \gg \Gamma_{exc}$ is always obeyed.

eration thresholds are very low (only about 50 watts). This was shown directly by the cited author, who could obtain laser action upon putting the sample, which was a typical Shpol'skiĭ system, in a resonator (a solution of coronene in a complex solvent at 100°K).

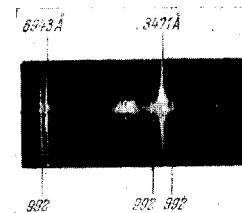
It is not clear at first glance why the discrete Shpol'skiĭ spectra are rather distinct. The exciting monochromatic line in a number of cases falls even in an interval between absorption lines, as can be judged from the literature data. Resonance stimulated Raman spectra are nevertheless not excited.

Perhaps the reason lies in the presence of a continuous component of the Shpol'skiĭ absorption spectra having an appreciable intensity. Apparently, the great power of the incident radiation, as well as the very low threshold for exciting Shpol'skiĭ emission spectra, favors this process that competes with stimulated Raman scattering. Moreover, the population of the lower triplet level also becomes significant, and transitions from the latter to the higher triplet state gives rise to absorption losses in the Stokes region of the stimulated Raman spectra.*

The effect on the stimulated Raman spectra of simultaneous irradiation of the substance by the original and converted laser radiations was also studied in^[36]. The authors calculated that one can neglect for anti-Stokes scattering the reverse (competing) process ($\nu_{anti-Stokes} \rightarrow \nu_{exc}$) when there is a stepwise mechanism of exciting stimulated Raman scattering in certain directions, owing to the specific angular intensity distribution. Thus, one can get amplification at anti-Stokes frequencies without satisfying the condition of synchronization.^[17] Here it was also assumed that the very powerful source laser radiation can substantially increase the population of the first vibrational level (to the point of saturation), owing to the Stokes stimulated Raman scattering that it excites. Thus it can lower the threshold for generating stimulated Raman scattering in the anti-Stokes region of the spectrum.

The experimental results have completely confirmed the starting idea. In particular, it has been found that an incident radiation of complex composition leads to excitation of anti-Stokes stimulated Raman lines, as well as Stokes lines. For example, in the stimulated Raman spectrum of frozen benzene, the anti-Stokes component proved to be almost as intense as the Stokes component, as we see in Fig. 13. Perhaps the appearance of the anti-Stokes lines is not only ascribable to the population of their initial vibrational state, but also to the conditions closer to resonance under which they are excited. As is well known, deviation of the intensity ratio

FIG. 13. Stimulated Raman spectrum of frozen benzene when simultaneously irradiated by converted and fundamental laser radiation.



*We assume that the centers responsible for the discrete and continuous components of the spectra interact.

$I_{\text{Stokes}}/I_{\text{anti-Stokes}}$ from the equilibrium value is one of the criteria of approach of spontaneous Raman scattering to the resonance region.^[14] Thus, apparently, true stimulated Raman scattering was observed in^[36] at the anti-Stokes frequencies, rather than parametric stimulated Raman scattering.

The fact that C—H bond vibrations are relatively easily excited in stimulated Raman scattering under quasi-resonance conditions can be explained on the basis of the theoretical calculations of Platonenko.^[19] As we have noted, this author showed that the threshold for generating stimulated Raman scattering can be proportional to the square of a quantity measuring the sharpness of resonance when there is no appreciable saturation and large vibrational quanta are being scattered. However, if these conditions are not satisfied, then the generation threshold proves to be independent of the closeness to resonance, as is implied also by the theory of Ananasevich and Ordabaev.^[2] Hence, resonance stimulated Raman scattering must have an especially effective influence on lowering the thresholds for generating the lines of C—H bond vibrations, since they correspond to greater frequencies.

The authors^[36] also measured the threshold for generating stimulated Raman scattering in certain polycrystalline substances. The measure of the threshold was the reciprocal of the limiting attenuation of a pulse, with use made of calibrated circuits.

It was found that the laser-action threshold of the C—H vibrations is twice as low as for the skeletal vibrations. For the latter, no explicit correlation was found between the size of the threshold and the closeness of the exciting line to the absorption band. In general, this agrees with the conclusions of Platonenko's theory.

Thus the results of the discussed studies imply that the process of resonance stimulated Raman scattering is extremely complex, and it cannot be described solely by taking into account the behavior of the spontaneous Raman spectra of the same substances. It is also evident that one can hardly achieve lowering of the thresholds for generating stimulated Raman scattering, nor increase the radiation conversion coefficient by the resonance effect. At the same time, it has been shown to be promising to use Shpol'skiĭ systems as sources of powerful discrete radiation and in studying vibrational transitions in ground-state and excited molecules during pulsed irradiation.

V. RESONANCE STIMULATED RAMAN SCATTERING OF EXCITED MOLECULES

The first report of such an effect is in^[10]. Solutions of cryptocyanine in glycerol vitrified at 77°K were studied at different concentrations of the substance. Figure 14 shows schematically the spectra obtained in^[10]. Emission lines are distinctly visible in the spectrum in Fig. 14 a at 530, 600, and 1005 cm^{-1} , as well as a narrow absorption line at 780 cm^{-1} . Furthermore, the laser-action band contains a coarser structure in which we can identify two broader absorption lines. As the solution is diluted, the laser-action band shifts to shorter wavelengths. At the same time, intensity is redistributed between the 530 and 600 cm^{-1} lines in favor of the latter, the 1005 cm^{-1} line vanishes, and

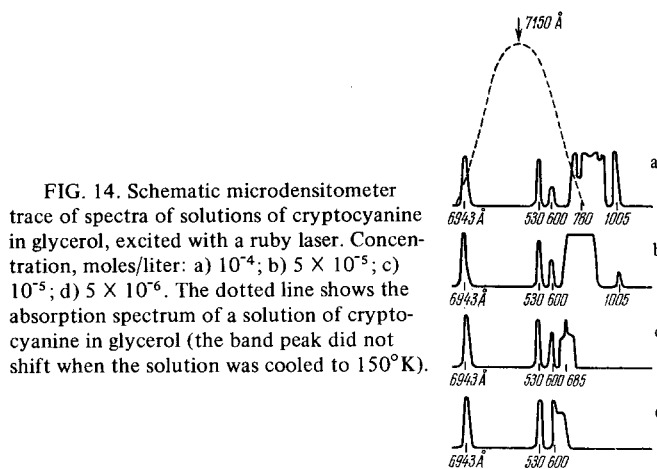


FIG. 14. Schematic microdensitometer trace of spectra of solutions of cryptocyanine in glycerol, excited with a ruby laser. Concentration, moles/liter: a) 10^{-4} ; b) 5×10^{-5} ; c) 10^{-5} ; d) 5×10^{-6} . The dotted line shows the absorption spectrum of a solution of cryptocyanine in glycerol (the band peak did not shift when the solution was cooled to 150°K).

in the spectrum in Fig. 14 c, a new line appears in the center of the laser-action band at 685 cm^{-1} .

The experimental results described above were obtained with a low-dispersion instrument. Study of the phenomenon on an instrument of considerably higher dispersion was needed to get information on the exact positions of lines in the spectra and to estimate their widths. This was done in^[11,13]. In particular, it turned out that the lines in the spectra are more or less broadened, sometimes unilaterally, and their width can be as great as $\sim 10 \text{ cm}^{-1}$. The latter fact led the authors of^[11,13] to perform experiments that directly showed the origin of the lines. The emission frequency of the laser was varied by varying the temperature of the ruby. The shift amounted to 4 cm^{-1} under the conditions of study in^[11,13]. The spectra belonging to different positions of the exciting line were photographed one under another on the same film with a fixed cassette. It was shown that all lines of the spectrum were shifted by the same amount, 4 cm^{-1} (Fig. 15).

Thus, these results unequivocally indicate that the spectra observed in^[10] are specifically to be ascribed to Raman scattering, rather than luminescence.

The problem was also to be elucidated of what levels and what diagram are involved in the Raman scattering.

The first idea is that the discussed studies observed resonance stimulated Raman scattering from the vibrational levels of the lower electronic state.* However,

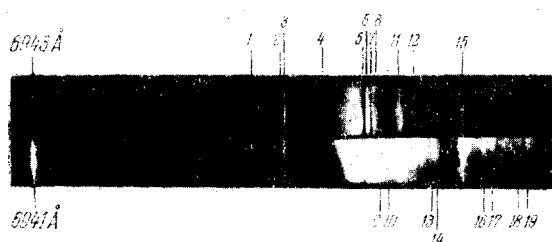


FIG. 15. Stimulated Raman spectra of a solution of cryptocyanine in glycerine ($C = 10^{-4}$ moles/liter), with a 2-Å variation in the wavelength of the exciting light.

*Resonance luminescence, i.e., a secondary-emission process that occurs without intermediate transitions in the excited electronic state, and is per se extremely improbable in a condensed medium, is ruled out by the results of studying the dependence of the positions of the lines in the spectrum on the frequency of the exciting light.

as we see from Fig. 14, the conditions are very unfavorable for such a process. At the initial instant of time, when the lower state is still populated well enough, the exciting line falls on the short-wavelength slope of the absorption band. This involves large losses in the Stokes region of the spectrum. Even the studies on resonance spontaneous Raman spectra have described only a few cases of this type.^[62] As the process develops further, practically all the molecules are transformed to the excited state, and this rules out scattering from the lower electronic level.

In principle, a case of scattering is not excluded in which the initial level is the first excited electronic level, while the intermediate level lies close to the next excited level. However, this requires fortuitous satisfaction of the condition of sharp resonance, which is quite improbable.

There remains a third variant of interpretation, consisting in the idea that the lines of the spectrum pertain to vibrational levels of excited molecules, while the transition itself occurs via a lower intermediate (virtual) state. We note in this regard that Yatsiv and his associates^[61] have apparently observed a three-photon scattering process having such an arrangement of the intermediate state involving the electronic levels in potassium vapor.

If this is so, then the fact is explained naturally that the appearance of lines in spectra depends directly on the concentration of the substance. In turn, the latter determines the conditions for laser action by the dye, or in other words, the position of its laser-action bands. Evidently, the Stokes lines in the spectrum resonate here with the laser-action band, and this is precisely the distinctive feature of a scattering mechanism by a "downward" system. At the same time, this emphasizes the stimulated character of the process. Moreover, this is also indicated by the threshold conditions for its appearance.

Nevertheless, control experiments were set up in^[11,13] in order to elucidate independently the role of the laser-action band in the observed phenomena. A third component, carbon disulfide, was introduced into the vitrified material. Its stimulated Raman line at 656 cm^{-1} fell within the laser-action band. It was compared with a specimen lacking cryptocyanine. Then no amplification of the stimulated Raman line of carbon disulfide was observed. Other experiments of this type will be described later. This means that the role of the laser-action band is not restricted to broad-band amplification of the line. Perhaps the very fact of its absence demonstrates the relative slowness of relaxation among the vibrational sublevels of the upper state, i.e., inhomogeneous broadening of the absorption band of the dye in the solid matrix. And this implies that it is possible in principle for discrete vibrational levels to be manifested in stimulated Raman spectra.

Undoubtedly, it would be of great interest to get independent data on the vibrational levels of the upper state and compare them with those found above. A direct method that gives such information is the Shpol'skiĭ effect in absorption. However, the literature contains no pertinent data, and perhaps the very choice of conditions for such an experiment encounters difficulties. Hence, the authors^[11,13] studied the infrared spectrum

Table I. Stimulated Raman and infrared absorption spectra of cryptocyanine

| Order No. | Vibrational frequencies (cm^{-1}), intensity estimates, and band widths | |
|-----------|--|---------------|
| | Stimulated Raman scattering | Infrared |
| | | 464 m, dif |
| | | 507 s, dif |
| | | 537 vs, dif |
| | | 575 s, dif |
| 1 | 535 w, sh | 615 m, dif |
| 2 | 606 w, sh | 625 s, sh |
| 3 | 612 s, sh | 655 w, dif |
| 4 | 700 w, dif | 703 m, dif |
| 5 | 785 s, sh (in absorption) | 758 vs, dif |
| 6 | 800 vs, dif | 792 vs, dif |
| 7 | 807 w, dif (in absorption) | } 816 m, dif |
| 8 | 816 } s, dif | |
| 9 | 831 } s, dif | } 863 s, dif |
| 10 | 848 } | |
| 11 | 870 s, v. dif | |
| 12 | 910 s, v. dif | 950 w, dif |
| 13 | 940 w, sh | } 990 w, dif |
| 14 | 950 vs, dif | |
| 15 | 1010 vs, dif | 1040 s, sh |
| 16 | 1055 m, dif | 1079 s, dif |
| 17 | 1075 m, dif | 1114 s, dif |
| 18 | 1132 w, dif | 1141 s, dif |
| 19 | 1150 m, dif | 1200 s, dif |
| 20 | 1163 w, dif | 1214 s, dif |
| | | 1225 s, dif |
| 21 | 1230 w, dif | 1237 s, dif |
| 22 | 1250 w, dif | 1296 vs, sh |
| 23 | 1343 vs, dif | 1327 w, dif |
| 24 | 1365 w, dif | 1373 vs, sh |
| | | 1477 vs, sh |
| 25 | 1548 } m, dif | } 1605 vs, sh |
| 26 | 1563 } | |
| 27 | 1585 } | |
| | | 2205 w, dif |

Notes: w—weak, m—medium, s—strong, vs—very strong, dif—diffuse, v. dif—very diffuse, sh—sharp. The numbering of stimulated Raman lines is the same as in Fig. 15.

of cryptocyanine, assuming that its set of frequencies should be similar, while their values should be somewhat larger, as usually happens. This is because the vibrations in this case pertain to the ground, rather than the excited state of the molecules.

The infrared spectrum was obtained by the tableting method with KBr over the range $400\text{--}2500\text{ cm}^{-1}$. Table I gives the measured frequencies. It also gives the frequencies of the stimulated Raman spectrum of the same substance. Comparison shows good agreement between the two sets. At the same time, we should note that the frequencies in the stimulated Raman spectra have as a rule somewhat smaller values, although the interpretation of the lines is not always indisputable. For example, a doublet with frequencies $604\text{--}610\text{ cm}^{-1}$ is typical of stimulated Raman scattering, while this clearly corresponds in infrared absorption to a band at $615\text{--}625\text{ cm}^{-1}$. Figure 16 shows some stimulated Raman spectra taken at high dispersion. Thus these data do not contradict the proposed interpretation of the stimulated Raman spectra.

Under forced conditions of excitation, one of the solid solutions of cryptocyanine showed an appreciably less intense laser-action band in the short-wavelength part of the spectrum, in addition to the intense band. This fact can be interpreted by taking into account the two stereoisomeric forms of excited cryptocyanine molecules.^[63] Since the weak band is excited only at maximum power of the incident radiation, we can conclude

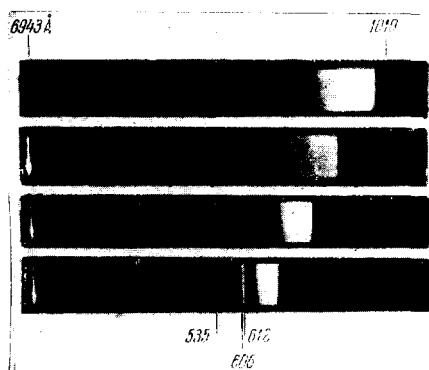


FIG. 16. Stimulated Raman spectra of glycerol solutions of cryptocyanine, as obtained upon varying its concentration from 0.5×10^{-5} to 10^{-4} moles/liter. The concentrations decrease from top to bottom.

that the content of the photostereoisomer responsible for it is small. Accordingly, it is shifted to shorter wavelengths (Fig. 17).

As for the absorption lines on the background of the laser-action band, we note first of all that their identification involves certain difficulties. One cannot always decide whether they are real or whether they are gaps between adjacent emission lines. In any case, one can interpret them as being inverse stimulated Raman spectra for the Stokes lines, i.e., ascribe them to the effect that Dumartin, Oksengorn, and Vodar^[64] has previously observed for an ordinary system of transitions.

Later it seemed possible to confirm the correctness of the proposed interpretation of the discrete part of the spectra described in^[13]. The technique used was to excite stimulated Raman scattering by ultrashort pulses (unpublished data obtained by the authors of^[13] jointly with V. V. Kryukov). The idea of the experiments is that, if one applies very fast excitation (with a pulse duration much shorter than the relaxation time among the vibrational levels of the upper state), then according to the discussed mechanism, stimulated Raman scattering should disappear, but luminescence will remain. A ruby laser operating in mode synchronization was used for the study. The laser generated about 10 pulses of duration of the order of 10^{-11} sec, each having a power of about 100 megawatts. Here only a very intense continuous laser-action band was actually observed, involving luminescence, while the discrete part of the spectrum vanished. The results of these experiments also completely rule out resonance luminescence as the reason for the spectral lines observed in^[13], although they can also be explained on the basis of resonance stimulated Raman scattering by unexcited molecules.

Thus, all the known criteria for resonance emission (apart from one that we haven't discussed, viz., ability to be quenched) are compatible with ascribing the dis-



FIG. 17. Stimulated Raman spectrum of a cryptocyanine solution obtained at maximum laser power and at a concentration of 0.5×10^{-4} moles/liter. The brackets indicate the different laser-action bands.

crete part of the discussed spectra to resonance stimulated Raman scattering occurring in a "downward" system.

An attempt was also undertaken in^[13] to measure the depolarization of the lines in the spectra. Since the studied compound is a highly conjugated system, it was assumed by analogy with scattering by the vibrational levels of the lower state that the depolarization of all the lines must be close to $1/3$ (with account taken of the fact that linearly-polarized light was used for excitation). It was also borne in mind that in this case one must compare the scattering spectra with luminescence, rather than absorption, in order to decide on their polarization states. Experiment showed that the stimulated Raman spectra are completely depolarized. This can indicate that the scattering tensor is complex, and that a magnetic-dipole component of the scattering tensor is complex, and that a magnetic-dipole component of the scattering is involved, or else, a very probable Jahn-Teller effect. It is also very likely that this feature simply reflects the strong stresses in the specimen that arise from rapid freezing.

In speaking of the line widths in stimulated Raman spectra, we must consider two different effects: homogeneous and unilateral broadening. As for the first effect, it can be naturally interpreted by the theory of Weisskopf,^[16] and specifically, it can be correlated with the short lifetime of the upper electronic (initial) state.

Unilateral (long-wavelength) broadening of the Stokes stimulated Raman lines can result from their resonance Rayleigh scattering, which leads to stimulated scattering of the wing of the line. The stimulated nature of the process is indicated by the distinct threshold observed in^[11]. Such an effect was first found for ordinary Rayleigh scattering (and outside a resonance region) by Fabelinskiĭ and his associates in liquids,^[65] and it has been investigated subsequently in other studies. The authors of^[66] have recently observed a Stokes broadening of stimulated Raman lines of the same type in unexcited molecules, but the spectra were excited by picosecond pulses. One argument in favor of the adopted assumption is that the exciting laser line itself in the experiments of^[11] did not undergo unilateral broadening. This means that Rayleigh scattering of the Stokes lines of stimulated Raman scattering by excited cryptocyanine molecules can occur when the conditions for resonance are satisfied. Another argument will be discussed below.

All of the interpretation of the results obtained in^[11,13] rests on the assumption of a latent vibrational structure in the absorption band of cryptocyanine, as has repeatedly been emphasized above. In view of this, it is reasonable to comment on the data of a study on the variation of the intensity of spontaneous Raman lines when excited within a broad electronic absorption band, as described in^[67]. The authors of this study showed that the greatest intensity of spontaneous Raman lines in the spectrum of p-nitrosodimethylaniline corresponds to the long-wavelength slope of the absorption band. If we assume that latent vibrational structure is a very widespread phenomenon, we can apply to this case the analysis performed by Krushinskiĭ and Shorygin. They treated scattering within a discrete absorption band,

and showed that the set of vibrational sublevels can be replaced by one or several effective sublevels on the long-wavelength slope of the absorption band, as regards their effect on the spontaneous Raman scattering intensity.^[68]

Moreover, the idea is not ruled out that sometimes it is more correct to interpret the frequency-dependence of the intensity of spontaneous Raman lines and the mechanism per se of the process in terms of Neporent's four-level concept, which takes into account relaxation processes of rearrangement of the nuclear configuration upon electronic excitation, and to treat an intermediate, unstable state of this model as the effective state.^[69] The latter is justified by the extremely short lifetimes of the virtual states and by the fact that the diffuseness of the vibrational sublevels apparently involves acquisition by the molecule of excess vibrational energy upon electronic excitation and subsequent exchange of this energy over the vibrational degrees of freedom.^[70]

While accepting resonance stimulated Raman scattering in a "downward" system as being the process that best corresponds to the facts observed in^[11,13] we must nevertheless not ignore other conceivable explanations of the phenomena. Figure 18 shows a diagram of a three-photon parametric resonance process of generation of vibrational quanta. It is analogous to that proposed by Kirsanov and Selivanenko,^[71] but differs from it in that the second intermediate level R_2 is also treated as a resonance level, corresponding to a vibrationally excited state of the lower electronic state. As in any other parametric process, it is essential here that the condition be satisfied of space-time synchronization of the light vectors of all three fields. Since illumination is carried out in the described experiments by a focused beam, and the scattered light has an appreciable aperture, it is always possible to find beams that satisfy the stated condition. Furthermore, in order to start such a generator, the quanta $h\omega_1$ and $h\omega_2$ must exist at the initial instant of time. The former gives the laser-action band of the dye, and the latter can be considered as noise. A necessary condition is that each of the transitions $R_1 \rightarrow R_2$ and $R_2 \rightarrow R_0$ should be allowed. This means that this process can create light quanta that are simultaneously active in Raman scattering and infrared absorption. Thus, centrosymmetric systems, over which alternating selection rules extend, will not work by this mechanism. Just as for ordinary two-photon resonance Raman scattering, a difficulty exists here, consisting of the fact that the exciting line at the initial instant of time (for cryptocyanine) falls on the long-wavelength slope of the absorption band. Hence, the Stokes lines should be strongly absorbed. Moreover, such a process can be responsible only for mani-

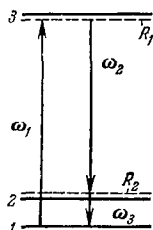


FIG. 18. Diagram of transitions for the case of a three-photon parametric resonance process.

festation of the vibrational levels of the lower electronic state. Exact theoretical estimates are needed for the efficiency of the process.

Study of resonance stimulated Raman scattering was further developed in^[12]. The objects chosen were, as before, cryptocyanine (DKI), and the related compound 1,1'-diethyl-2,2'-dicarbocyanine iodide (DDI), crystallized in different matrices: acetone, tetrahydrofuran, and dimethylformamide. It was considered that use of crystallizing solvents (as compared with glass-forming solvents) should lead to still greater narrowing of the vibrational levels that would favor generation of stimulated Raman scattering. Moreover, it was considered that the specific features of the crystalline field would be manifested in the spectra upon varying the solvent. It was also proposed to compare the structure of the scattering lines when excited under various environmental conditions.

As before, more or less broad laser-action bands of the dye were observed in^[12], along with a discrete component of the stimulated Raman spectrum. Figures 19 and 20 show specimens of typical spectra. Table II* gives the data in full.

We see that the obtained spectra contain extremely narrow lines of various intensities. Comparison with the data for DKI shows that these lines fundamentally agree well in their positions with the broader lines that are characteristic of vitrified specimens.^[13] Moreover,

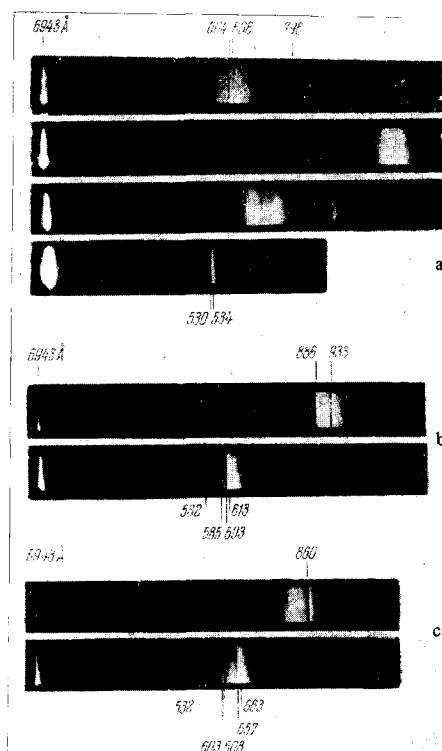


FIG. 19. Regions of the spectra of crystallized solutions of DKI: a) in acetone; b) in tetrahydrofuran; c) in dimethylformamide.

*As before, irradiation of the matrix by a powerful ultrashort laser pulse led to disappearance of the narrow lines of the spectrum. The laser-action band of the dye remained.

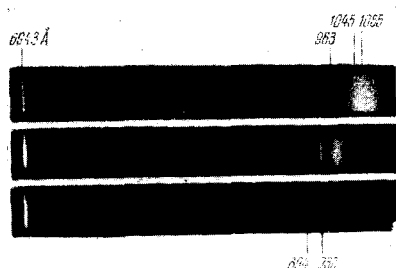


FIG. 20. Regions of spectra of crystallized solutions of DDI in tetrahydrofuran. The concentration decreases from top to bottom.

it turned out that the spectra of the latter are appreciably richer in lines, and extend as far as vibrational frequencies of $\sim 1600 \text{ cm}^{-1}$. This can be associated with the already mentioned stereoisomerism of the excited molecules, since an energetically less stable isomer cannot be formed upon crystallization and pumping of the solution. The stimulated Raman spectrum is consequently simplified.

The positions of the stimulated Raman lines of the studied dyes varies to different extents as a function of the crystalline matrices used. New lines appear, while some lines are split.* The behavior of the line near $\sim 530 \text{ cm}^{-1}$ in the spectrum of DKI is especially striking. While it is relatively diffuse in a system containing tetrahydrofuran or dimethylformamide, it splits into two components in an acetone system (Fig. 21). This indicates differences in the crystal field of the matrix.

Very interestingly, an absorption line or band adjoins certain of the emission lines on the anti-Stokes side. We can understand the nature of this phenomenon if we take into account the inhomogeneous broadening

FIG. 21. Regions of spectra of crystallized solutions of DKI: a) in tetrahydrofuran; b) in acetone. Splitting of the line into two components can be seen.

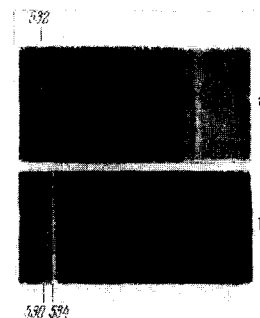
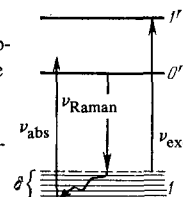


FIG. 22. Diagram of transitions explaining the appearance of absorption on the short-wavelength side of the stimulated Raman line. For simplicity, the broadening of the vibrational levels of the excited state is not shown. δ is a measure of the inhomogeneous broadening of the lower level.



of the vibrational levels of the lower state arising from the existence of different emission centers. Figure 22 shows a diagram in exaggerated form. We see that Raman scattering occurs as soon as the arrow, which imitates a luminescent transition, reaches the upper component of the inhomogeneously broadened vibrational level, since then a sharp resonance is realized, and Raman scattering occurs within an extremely short interval of time. Later, the system relaxes, and the lower component of the discussed level from which light absorption occurs acquires a non-equilibrium population. Thus, the shift of the emission line with respect to the absorption line that adjoins it characterizes the

Table II. Stimulated Raman spectra of DKI and DDI crystallized in various solvents

| DKI | | | DDI | | |
|---------------|--------------------|----------------------|------------|--------------------|----------------------|
| in acetone | in tetrahydrofuran | in dimethylformamide | in acetone | in tetrahydrofuran | in dimethylformamide |
| 290 w, v. dif | 510 w, dif | | | | |
| 530 m, br | 532 s, dif | 532 m, dif | | | |
| 534 s, sh | | | | | |
| 560 w, dif | 585 w, sh | | | | |
| 604 } s, sh | 603 } s, sh | 603 } m, dif | | | |
| 608 } | 613 } | 608 } | | | |
| | 665 w, sh | 657 } vs, sh | | | |
| | | 663 } | | | |
| 695 w, dif | 695 w, dif | | 800 m, sh | | |
| 795 m, sh | | | | | |
| | 835 w, sh | | | 835 vw, sh | |
| | | 860 vs, sh | 848 m, dif | | |
| | 877 vw, sh | | 875 w, dif | | 870 vs, sh |
| | 886 vs, sh | | | 894 vs, sh | |
| | | | 913 m, dif | | |
| | 933 vs, sh | | | 932 vs, dif | 926 } vw, sh |
| | | | | | 935 } |
| | | 1030 w, dif | | 963 w, sh | 945 vw, sh |
| | | 1040 w, dif | | 1045 s, sh | |
| | | | | 1065 w, sh | |

Notes: The numbers are the frequencies of the lines in cm^{-1} ; vs—very strong, s—strong, m—medium, w—weak, vw—very weak, sh—sharp, dif—diffuse, v. dif—very diffuse, br—broad.

*In some cases, the splitting components can be ascribed to Weisskopf "anomalous" scattering, as discussed above.

width of the vibrational level, while the absorption itself arises from an induced process.

The concentration-dependence of the shift in the laser-action band of DKI dissolved in tetrahydrofuran or dimethylformamide is the usual one: the band shifts to shorter wavelengths with decreasing concentration of the substance. A peculiar feature is observed in the behavior of an acetone solution. As the concentration is decreased from the maximum value, the band first shifts to longer wavelengths, and then reverses in direction. At low concentrations, a relatively narrow satellite appears on the long- or short-wavelength side, alongside the main band. The satellite is separated from the laser line by only 250 cm^{-1} (see Fig. 19).

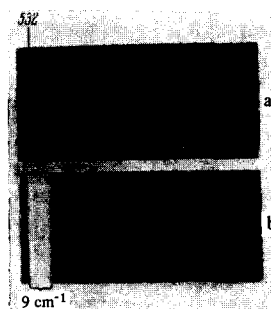
We can try to interpret the anomalous shift in the laser-action band of DKI in acetone solutions as follows. We shall take into account two observations known from the literature: a certain narrowing of the absorption bands of the substance in dilute crystalline solutions, even in polar solvents; and the diffuseness of the discrete Shpol'skiĭ spectra under conditions in which the concentration of the substance is below some optimum value. In this case, the simultaneous effect of the two phenomena can have the result that dilution of the DKI with acetone initially increases the absorption in the region of laser emission, owing to broadening of the band. Thereupon, the dilution process predominates, and the absorption begins to decline. Correspondingly, the laser-action band does not show a monotonic shift.

As we have noted, DDI is related in structure to DKI, and differs from it only in the length of the chain of methine groups and the way in which it is attached to the quinoline rings. Hence the spectra of the two substances are similar, although the frequencies of the lines do not exactly coincide (see Table II). As before, the effect of the solvents on the stimulated Raman spectrum is appreciable. The lines of the stimulated Raman spectrum have analogs in the infrared spectrum of the same substance. For example, the stimulated Raman lines in the region $870\text{--}895\text{ cm}^{-1}$ correspond to an infrared band of medium intensity at 902 cm^{-1} . The group of lines at $913\text{--}932\text{ cm}^{-1}$ correspond to a weak band at 950 cm^{-1} , etc. As before, we can naturally ascribe the higher frequencies of the analogs in the infrared spectrum to the fact that the latter pertain to the electronic ground state. The positions of the laser action bands as a function of the concentration show no anomalies.

Remarkably, the stimulated Raman spectrum of DDI vitrified in alcohol shows two weak, diffuse lines of frequencies 835 and 913 cm^{-1} , just as in a crystallized matrix. However, the very intense lines typical of the latter are lacking.

It is of some interest to study mixed solutions of different dyes. This has been done in^[12] with the example of a crystalline matrix in tetrahydrofuran, with various ratios of DKI and DDI introduced into it. At relative contents of these dyes of 4:1 and 8:1, respectively, only the lines of the latter dye (894 and 932 cm^{-1}) and its laser-action band were manifested in very intense form, although the concentration of DKI and the position of the laser-action band of DDI would seem to favor excitation of the DKI line at 886 cm^{-1} . When the content of DKI in the solution predominated considerably (40:1), its lines at ~ 610 and 796 cm^{-1} were mani-

FIG. 23. Regions of spectra: a) a crystallized solution of DKI in tetrahydrofuran; b) a vitrified solution of DKI in glycerol. Unilateral broadening of the lines can be seen in the latter case.



festated weakly, while the 894 cm^{-1} line belonging to DDI was very intense and sharp. Evidently, these results indicate that: first, the dyes compete (one dye interferes with laser action in the other)*; second, there is no broad-band amplification of the lines in the laser-action band. This confirms our ideas on the role of the laser-action band in the phenomenon studied in the articles cited above.^[11-13]

Let us return to the problem of the unilateral broadening of stimulated Raman lines in the spectra of vitrified cryptocyanine. It has been interpreted as a manifestation of resonance Rayleigh scattering. If this is true, then evidently, the effect must be absent in crystallized matrices in view of the rigid fixation of the molecules in the crystal structure. In full agreement with our expectations, the wing in the Stokes stimulated Raman lines of such systems is actually absent, as is quite evident in Fig. 23.

VI. CONCLUSION

The types of interaction of powerful radiation with matter are highly varied. Many-quantum processes, including stimulated Raman scattering, have acquired a great scientific-perceptive and purely utilitarian importance. Until now, people have known and studied intensively only stimulated Raman scattering in the region of transparency of molecular systems. This review presents the first results on another case of stimulated Raman scattering in which the frequency of the exciting radiation approaches the region of intrinsic absorption of the substance. And even though experiment shows that resonance conditions of excitation do not lead to a sharp lowering of the laser-action threshold (an effect that would have valuable practical applications), such studies are still of no little interest in connection with testing and further development of the theory of this phenomenon, and with extending and deepening our understanding of the concomitant processes. As we have tried to demonstrate, resonance stimulated Raman spectra generated by non-trivial quantum transitions via a lower intermediate (virtual) state can give extremely important and unique information on the vibrational transitions and properties of molecules in electronic excited states.

*DDI is distinguished by a very high radiation-conversion coefficient in liquid solutions (data of T. K. Razumova).

Note added in proof: Theoretical and experimental results on resonance stimulated Raman scattering have been reported at an international symposium in Dresden (K. Lenz, A. J. Weigman, M. Pfeiffer, A. Lau, W. Werncke, and P. Gadow, Int. Tagung "Laser u. ihre Anwendung", Deutsche Akad. d. Wiss. zu Berlin, Inst. f. Opt. u. Spektroskopie, Abstracts, 1970, p. 62). I. K. Kvitoishvili, M. V. Melishchuk, E. A. Tikhonov, and M. T. Shpak have observed discrete spectra in the liquid phase of a substance (5th All-union Conference on Non-linear Optics, Kishinev, November, 1970, Abstracts, p. 89).

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