### Recent progress in dynamical spectroscopy of Raman light scattering

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The physical bases and some features are presented of the different methods of time-resolved Raman spectroscopy, and also different variants of their realization. The concrete results of the studies are discussed with a large number of examples, including problems of the course of a number of photochemical and photophysical processes and of the structure of intermediate and final products formed under exposure to optical pumping or electron impact. The review also includes data, obtained by using the same spectroscopic methods, on the effect on matter of high-power dynamical loads. Special attention is paid to intrapulse stimulated Raman scattering, which reveals the behavior of the vibrational modes in real time. The further prospects of the development of the latter method and its possible sphere of new applications are analyzed.

### **1.INTRODUCTION**

Dynamical spectroscopy is usually taken to mean the field devoted to studying the decay and dephasing of vibrations, the movement of the population of excited levels, energy transport, and also the structure of short-lived complexes whose existence is due to the action on a system of external fields, mainly optical pumping fields. Often such studies are accompanied by kinetic measurements that yield additional information on the processes that are occurring.

The beginning of dynamical spectroscopy goes back to the method of pulse photolysis, which was first realized at the end of the forties, and which immediately became recognized and widespread.<sup>1</sup> Already in its initial realization using flash lamps, it proved suitable for identification (from the absorption spectra) of intermediate products of phototransformations in a time interval from milliseconds to fractions of microseconds. The advance toward studying considerably faster processes was stimulated by the invention and adoption into laboratory practice of lasers, which generate sufficiently powerful light pulses of durations down to tens of femtoseconds at very high repetition rates and over a broad range of wavelengths.<sup>2</sup> The progress in this very important field continues.

However, in many cases the absorption spectra are composed of very broad, structureless bands, and this substantially reduces the amount of obtainable information on the instantaneous composition and structure of the material. For this reason, different variants of Raman spectroscopy, and primarily, spontaneous Raman spectroscopy, began to be applied for probing systems in concrete situations. For example, by using this method, already about twenty years ago, the very interesting studies of triplet molecules<sup>3</sup> were begun and are continuing now. In recent years studies have started of molecules converted into the first excited singlet state, whose lifetime is considerably shorter, which leads to additional difficulties. In the various experiments the system was pumped, as a rule, with radiation at one frequency, and was probed with radiation at a different frequency lying in optical resonance with the new complexes, thus sharply and selectively increasing the intensity of the probe signal. Moreover, the probe pulse was applied to the medium with a regulated time lag (pause), whereby it was possible to obtain spectra with the maximum population of the corresponding

excited state, i.e., under optimized experimental conditions.

Since the transitions in Raman scattering involve participation of virtual levels whose lifetime is of the order of  $10^{-15}$  s, for this reason alone any methods of time-resolved spectroscopy that use Raman scattering signals for probing a system would seem to be considered the best. As regards spontaneous Raman scattering, this conclusion is only partly true. The point is that spontaneous Raman scattering amounts to an extremely low-efficiency process of conversion of radiation, and one cannot always increase its cross section via resonance, if only because it is often accompanied by a luminescent background. On the other hand, application of spontaneous Raman scattering to study very fast processes involves a difficulty in principle, namely, that, owing to the quantum-mechanical uncertainty relation, all the spectral lines of the short probe pulse are broadened. Thus one loses the opportunity of simultaneously realizing high time and spectral resolution of the signals. This compels experimenters on this problem to make certain compromises, depending on the character of the problem to be solved.

While one uses nonlinear methods in dynamical-spectroscopy experiments, the preparation of coherent vibrational states can be performed by various means. Let two light pulses be incident on the system with different intensities and wave vectors  $\omega_1$ ,  $\mathbf{k}_1$  and  $\omega_S$ ,  $\mathbf{k}_S$ . When they coexist in space and time in the system, coherent vibrations are pumped that form a running wave  $\omega_0 = \omega_1 - \omega_S$ ,  $\mathbf{k} = \mathbf{k}_1 - \mathbf{k}_s$ , where  $\omega_0$  is one of the active vibrational modes intrinsic to the specimen, in which the process of stimulated Raman scattering develops. This is selective in character and does not require overcoming a power threshold for its appearance, as is characteristic of "classical" stimulated Raman scattering. Here the weak radiation at the frequency  $\omega_{s}$ is amplified by the more powerful radiation at  $\omega_1$ . From the practical standpoint it is very important that the initiation and maintenance of the process of this stimulated Raman scattering can be effected with a long train of relatively lowpower pulses. One can trace the time behavior of the coherent vibrations, as before, by using probe pulses with appropriate delays.

Recently the authors of Ref. 5 described examples of successful application of another method of exciting stimulated Raman scattering and probing a system for studying dephasing of vibrations. It was first proposed by the author of Ref. 6 in 1979 and is based on using two synchronously pumped lasers based on liquid dye solutions. Information on the vibrational relaxation was extracted from the dependence of the intensity of the Stokes component on the lag time.

A method is also known of creating a nonequilibrium population of the first excited vibrational level owing to direct absorption of sufficiently powerful laser infrared pulses or as the result of development of single-pulse (threshold) stimulated Raman scattering.<sup>7</sup> This method enabled performing a series of important studies of hot phonons in a number of media by using not only Raman scattering, but also hyper-Raman scattering.<sup>8-10</sup>

Very often the dynamical behavior of a material is studied by using a frequency variant of coherent anti-Stokes scattering (CARS) with broad-band pumping. This allows one, without frequency scanning, to measure directly a rather broad region of the spectrum that bears the necessary information on the composition and structure of the intermediate products, as formed, e.g., in a process of pulse photolysis or radiolysis. In this regard we focus attention on certain features of CARS spectroscopy, while referring the reader for obtaining exhaustive information on all the physics and technology of this remarkable method to the review and monograph<sup>11</sup> and to the references contained therein on the ground-breaking studies in this field.

As is known, in the presence of an electromagnetic field the medium is polarized. In the general case the polarization vector in symbolic notation can be represented as a power series in the field  $E(\omega)$ :

$$P(\omega) = \chi^{(1)} \cdot E(\omega) + \chi^{(2)} : E^2(\omega) + \chi^{(3)} : E^3(\omega) + \dots \quad (1.1)$$

The coefficients  $\chi^{(i)}$  are called the dielectric susceptibilities and are respectively second-, third-, and fourth-order tensors. In weak fields the term of the expansion (1.1) that is linear in the field (the first term) plays the essential role. It describes the linear optical effects, in particular, Raman scattering. When high-power laser fields act on the medium, one must now deal with the contribution to the polarization of the medium of the higher (nonlinear) terms of the expansion. Here it turns out that the term quadratic in the field is responsible for such processes as frequency doubling, generation of sum and difference frequencies, the simplest parametric interactions, and hyper-Raman scattering. It differs from zero for systems having no inversion symmetry. That is, as is known, rules out of discussion gases and liquids, for which we always have  $\chi^{(2)} = 0$ . Finally, the third term in (1.1) (written in expanded form as  $\chi_{ijkl}^{(2)}$ ) for all media, including isotropic ones, is the source of information on more complex processes in which several light waves with different frequencies are involved.

In connection with problems of dynamical vibrational spectroscopy, the case is especially interesting of the active influence of such waves on the medium when the difference of their frequencies is close to one of the vibrational modes allowed in Raman scattering, i.e., the case of resonance. Here, depending on the concrete experimental scheme, one can observe a number of related problems described by the same tensor, but with a different combination of subscripts. Among them, CARS spectroscopy has been most widespread up to now. The cubic susceptibility of the medium can be written as the sum of two terms

$$\chi^{(3)} = \chi^{(3)R} + \chi^{(3)NR}, \qquad (1.2)$$

Here the first term reflects the contribution of vibrational resonance caused, as was noted, by the coincidence of the difference between the frequencies of the incident radiations with the frequency of a chosen mode, while the second term is associated with nonresonance (in the same sense) vibrational transitions, such as those provided by the pure electronic contributions of the solvent and buffer gas, as well as by remote vibrational levels of the working medium itself.

In turn, the resonance term in (1.2) amounts to the complex quantity

$$\chi^{(3)R} \neq \chi^{(3)'} + i\chi^{(3)''}. \tag{1.3}$$

Thus we finally have

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$$\chi^{(3)} = \chi^{(3)'} + \dot{\chi}^{(3)''} + \chi^{(3)NR}. \qquad (1.4)$$

It is very important precisely which component of the susceptibility, the imaginary, the real component, or their moduli governs the process being discussed. The case is most favorable in which this is the imaginary component. It corresponds to excitation of stimulated Raman scattering. In particular, CARS is described by the square of the modulus of  $\chi_{ijkl}^{(3)}$ . Thus interference effects are introduced into the spectra, which restrict the sensitivity of the method, and distort the form of the output signal.

In experiments in CARS spectroscopy a four-wave parametric mixing is realized of the type  $\omega_{AS} = 2\omega_1 - \omega_S$ , which yields at the output a signal whose intensity is proportional to the square of the cubic susceptibility  $\chi^{(3)}$  and the square of the number of scattering centers. The parametric character of the process of mixing the acting light waves predetermines the direction of observation of CARS spectra in which the most complete energy conversion of these waves is effected, and, which therefore, also corresponds to the maximum value of the recorded signal, which is dictated by the requirement of maintenance of their space-time synchronization. If we neglect the dispersion of the medium, this direction amounts to an angle of 0° with respect to the pump beam.

The theoretical analysis of the processes that lead to formation of the CARS spectrum is reduced to determining the amplification in space of the wave  $\omega_{AS}$ . One writes an expression for the component  $\chi^{(3)}$  of the polarization of the medium under the action of the fields  $\operatorname{Re}(E_1 e^{-i\omega_1 t})$  and  $\operatorname{Re}(E_S e^{-i\omega_S t})$ , and solves the Maxwell equations. After integration and using the known relationship between the electric field intensity and the intensity of the radiation  $I_i = (C/8\pi^2)|E_i|^2$ , the relative amplification  $\varepsilon$  (i.e., the efficiency of the conversion process) is expressed in terms of the fundamental parameters as follows:

$$\varepsilon = \frac{I_{AS}}{P_S}$$

$$= \left(\frac{4\pi^2 \omega_{AS}}{n_{AS} C^2}\right)^2 |3\chi^{(3)}(-\omega_{AS}, \omega_1, \omega_1 - \omega_S)|^2 P_1^2 L^2 \left[\frac{\sin(\Delta kL/2)}{\Delta kL/2}\right]^2.$$
(1.5)

Here  $P_i$  is the power of the corresponding beams, L is the interaction length, and  $n_{AS}$  is the refractive index at the frequency of the anti-Stokes transition. The quantity in square brackets is determined by the conditions of synchronization of all the waves. We see the quadratic dependence on the modulus of the susceptibility  $\chi^{(3)}$ , of the intensity  $I_i$  of one of the radiations being mixed, and of the interaction length L (the concentration of the material). All this taken in combination complicates the spectral pattern and the interpretation of the results themselves. Also an unequivocal analytic relationship is defined between the intensity in CARS spectra and the cross section of spontaneous Raman scattering.

Turning to the overall properties of the CARS method, we note the following. The radiations in CARS spectra are converted far more efficiently than in spontaneous Raman scattering (for transparent substances by a factor of up to  $\sim 10^5$ ). Generally one can observe CARS spectra without using a spectroscopic instrument. Here the attainable resolution is completely determined by the width of the lines of the lasers employed. It can amount to values from hundredths to thousandths of a reciprocal centimeter. In the converse case, i.e., using a spectroscopic instrument, it is precisely the optical parameters of the latter that impose the resolution limit. In particular, the technology of CARS spectroscopy allows using pulsed lasers, which plays the determining role in the context of the theme of this review, while their power requirements are moderate. Since, finally, the signal detected in the CARS method lies in the anti-Stokes part of the spectrum, even this removes to a considerable extent the difficulties of studying luminescent media. Additional possibilities of suppressing luminescence consist in the narrow directionality of the output signal of CARS (whereby it is distinguished from luminescence). This enables one to diminish the interference due to it by spatial separation of the working cuvette and the receiver.

A cardinal defect of the CARS method has already been noted above-the existence in the spectra of a background due to the nonresonance (in the sense of the closeness of the pump frequency to the vibrational levels of the system) nonlinear susceptibility  $\chi^{(3)}$ , which is manifested in the form of a background formally analogous to the luminescence background in spontaneous Raman spectra, which not only reduces the sensitivity of the method, but also distorts the form of the output signal. The means of weakening interference of this type can prove to be an appropriate choice of the polarization of the interacting waves. In the practical respect, the complexity of the entire complex of apparatus, which further requires delicate and stable adjustments, is of essential significance for applications of CARS spectroscopy to problems of studying the dynamical properties of materials.<sup>11</sup> Moreover, certain difficulties in quantitative measurements with CARS spectra involve the sharp dependence of the magnitude of the output signal on a number of parameters that are not easy to control. Its fluctuations commonly amount to  $\sim 20\%$ .

In the time-variant modification of CARS spectroscopy the system is tuned rigidly to the chosen vibrational mode, while the variable quantity is the pause between the pump and probe pulses. It goes without saying that, the physics of the process of forming the output signal is completely maintained.

To study various dynamical problems, another nonlin-

ear optical method has been applied in a number of studies, which is called in the foreign literature the Raman induced Kerr effect, or RIKE.<sup>1)12</sup> Its essence and fundamental scheme of experimental realization consist in the following.

Two light beams are made to coincide in a restricted volume of the specimen. One of them (relatively powerful) serves as the pump. It can be narrow-band<sup>12</sup> or broadband.13 A weak radiation of some particular spectral composition fulfills the functions of the probe. It is polarized linearly, while the pump is circularly polarized. The output signal is transmitted through a polarizer that picks out the perpendicular component. Here the pump beam is directed aside. Since the pump induces a Kerr effect at the frequency of an active Raman transition, i.e., an optical anisotropy, the system in the direction of observation proves not to be closed and transmits the component of the radiation at this frequency. Here its intensity is determined by the combination of a number of factors-the sharpness of the vibrational resonance (i.e., the coincidence of the difference  $\omega_1 - \omega_s$  with the maximum of the vibrational mode), the properties of the corresponding levels and transitions between them, and also, of course, by the power of the pump itself. The process being discussed, just like CARS, is described by the nonlinear susceptibility tensor  $\chi^{(3)}$ , but with another combination of indices. In contrast to CARS, an internal fulfillment of spacetime synchronization of the light beams is inherent in this effect. Therefore, RIKE can be observed generally at arbitrary angles.

To the defects of this method, which are, by the way, also characteristic of CARS, and which involve interference effects, is added also the great sensitivity of the measurements to the depolarizing action of the optical details of the apparatus. Moreover, a spectroscopic instrument is always necessary for experimental realization, which involves additional difficulties in obtaining high resolution.

New and greatly promising pathways of development of time-resolved Raman-spectroscopy, and also transitions to electronically excited states of various systems have been noted in recent years after another possibility of optical generation of vibrations had been achieved. In the initial variant of the experiment, two intersecting pump light beams were applied to the specimen, formed by single pulses from the same laser, whose duration  $\tau$  satisfied the condition  $\tau < 2\pi/\omega$ , where  $\omega$  is the frequency of the chosen optical mode. Thus, depending on the magnitude of the latter,  $\tau$  can lie in the range of values from units to tens of picoseconds (the components of the Mandel'shtam-Brillouin scattering, certain acoustic modes) to the now-accessible tens of femtoseconds (vibrational optical modes with relatively low frequencies). Under the circumstances being discussed, the results for a number of dyes and semiconductors were found in the form of quantum beats at the edge of transmission bands.<sup>14–18</sup> It is considered that the fact of appearance of these beats is due to interference of close-lying states pumped coherently owing to their overlap by the broadened ultrashort pulse. A number of other methods of preparing coherent states in molecular and atomic systems is possible, also detectable in the form of quantum beats (see, e.g., Ref. 19).

In approaching the problem of the nature of quantum beats from other theoretical standpoints, the authors of Refs. 20–30 have generally applied a single-beam scheme to excite coherent modes, while as before the system was probed with pulses of the same duration from the same laser, but with a time lag. Here the pattern obtained with them was interpreted in terms of stimulated scattering, in particular, stimulated Raman scattering. We shall call the corresponding processes intrapulse processes. It was shown that they are inherent in equal degree in each of the two experimental schemes. In a number of studies, the specifics of the course of intrapulse stimulated Raman scattering and certain other problems typical of transparent and absorbing media have been discussed. Great advances have been made also in the experimental respect, and also new spheres of application of the method have been found, e.g., in studying intermolecular interactions.<sup>26,27</sup>

Thus the spectroscopy of intrapulse stimulated scattering has already become a very important source of information on the vibrational dynamics of liquids and solids in real time. Earlier, indirect data of the same sort were extracted from the contour of vibrational bands, in particular, Raman scattering, excited under steady-state conditions. Here serious fundamental difficulties arose in identifying the sought time characteristics, if only for the reason that generally the analytical bands suffer from inhomogeneous broadening, and doubts could always arise regarding the correctness of the treatment of the experimental results, i.e., their unambiguous assignment to relaxation rates or to dephasing of vibrations. Moreover, the accuracy of the measured quantities was usually limited by the low values of the signal to noise ratio. Nevertheless, the problems of the influence of fast processes of structural rearrangement (rotation of individual fragments, ring opening, dissociation) in electronically excited molecules on the electrooptical characteristics of their usual spontaneous Raman and CARS spectra continue to attract attention of theoreticians and experimentalists, to which, e.g., Refs. 31-33 are devoted.

Of course, problems of the sensitivity and accuracy of the measurements arise in many dynamical experiments. To improve these parameters of the working apparatus wherever possible, Raman spectra are excited with a very long train of laser pulses, which are sometimes compressed in time, amplified, and a broad continuum is excited with them. which ultimately serves to pump the systems being studied.<sup>17</sup> But we must not lose sight of the fact that this method is applicable only when the duration of the pulses is greater than  $\sim 150$  fs, while their repetition rate amounts to several kilohertz or less. Even the first condition is unacceptable, since it limits the possibility of studying ultrafast processes. An apparatus has proved practical that uses pulses of arbitrary duration (down to tens of femtoseconds), but with a repetition rate up to  $\sim 50$  MHz, which ensures a good signalto-noise ratio owing to averaging of a vast number of measured signals.17

the literature cited there). Nevertheless, one still finds publications devoted to the study of the structure and properties of anion and cation radicals as intermediate products of photophysical and photochemical radiolysis processes.

For many reasons it seemed fully appropriate and logical to include in the review the results that pertain to studying transformations of matter that set in when powerful dynamical loads are applied to it, i.e., its instantaneous structural state under real experimental conditions. In recent years a tendency has become prominent to extend also to this field the methods of time-resolved spontaneous Raman spectroscopy and CARS, in the latter case in the broadband pumping variant. Consequently we now have not only a theoretical, but also a certain methodological generality of the entire outlined set of problems, in particular also because shock experiments require temporal (and ultimately spatial) synchronization of the probe light beam with the front of the shock wave.

The studies noted above open up a direct pathway to solving a multitude of problems of fundamental importance concerning molecular dynamics and the thermodynamics of condensed media, synthetic chemistry, etc., and also have the prospects of application in a purely military respect, in which the objects are explosives. It is also very important that powerful radiation pulses, especially under conditions of appreciable absorption also lead to the appearance in the specimen of shock waves. This must make its imprint also on single-pulse stimulated Raman spectra. Independent data are needed to judge on the character of these influences.

Thus, in the field of dynamical Raman spectroscopy understood in the broad sense, outstanding results have been attained at present. It lies far outside the framework of this review to describe them. Our attention will be concentrated only on the newest problems, which in the author's opinion are of fundamental spectroscopic interest and are very important in a multitude of allied fields of science and technology.

In closing we note that the English-language literature generally uses two terms to denote the methods of time-resolved spectroscopy: "Pump-and-Probe Technique" and "Time-resolved Spectroscopy." Sometimes one encounters the less exact expression "Two-Color Methods."

### 2. SHORT-LIVED ELECTRONIC-VIBRATIONAL SYSTEMS 2.1. Resonance spontaneous Raman scattering: triplet and singlet excited molecules, and ionic forms of them

As is known, the cited compounds often determine to a considerable extent the course of many photochemical reactions. In this sense an especially important role belongs to triplet molecules, which are usually detected by phosphorescence, by  $T_1 \rightarrow T_2$  absorption spectra, or from EPR signals.<sup>4</sup> Since the lifetime of the levels  $T_1$  is large, one can populate them rather effectively, whereby the prerequisites have been created for planning the first experiments to use spontaneous Raman scattering specifically as a method of identifying and establishing the structures of triplet molecules.<sup>3</sup> Later this method became extended to the case of studying other intermediate products of the photodecomposition of materials, such as molecules in the first singlet excited state and in various anionic and cationic forms. Consequently dynamical spectroscopy, which was based on using the effect of reso-

nance spontaneous Raman scattering to probe systems, was converted rather long ago into the principal means of studying various aspects of the problems of photophysics and photochemistry of matter.

Of the two existing methods of converting molecules to the triplet state—by photoexcitation or by radiolysis (pulsed electron impact)—most authors apparently prefer the first of them, this being associated with the cleanness of the corresponding experimentation. Later this statement will be illustrated with a single example. On the other hand, the possibilities of realizing photoexcitation and subsequent probing of the system at the attained level of development of laser technology are so varied as to permit performing studies of practically any substances, and over a broad spectral range. All the details and features of the experimental means applied at present will be given in the context of a brief presentation of the concrete results of the multitude of selected publications, together with the motivation of the planning of the studies itself.

This section (and also further on) will preferentially treat studies performed in recent years. Selected data on studies of the earlier period will be presented only to the extent needed to show the general tendencies and paths of development of time-resolved spectroscopy of light scattering. As regards the present section, a complete description of all the very extensive factual material can be found in the proceedings of various conferences and in monographs.<sup>36–39</sup>

A remarkable feature of the flow of published papers on the theme in which we are interested is the choice of objects of study, which are important in many allied fields of knowledge and in technology, whereby the progress in these special fields has been stimulated. Such, in particular, are biological objects, to which a large number of publications has been devoted.<sup>39</sup> On the other hand, the fact merits attention of the systematic updating of the technical means of experimentation—pump and probe sources for systems, as well as the entire complex of receiving and recording apparatus and the corresponding measurement procedures. In turn, this feedback enables one to formulate and solve new problems. An especial place is taken here by the application of femtosecond laser pulses.

To illustrate the varied analytical potentialities of the method being discussed, we shall give in condensed form a summary of certain typical results.

Bacteriochlorophyll a plays an important role in the course of the processes of photosynthesis in bacteria. To elucidate it requires a knowledge of the structure of these molecules in the triplet state. However, the difficulty of obtaining spectra under resonance conditions of excitation involves the photosensitivity of the substance. Moreover, the content of oxygen in the working solution exerts a strong influence on the state of the latter. To exclude these side effects, the authors of Ref. 40 conducted the study in an evacuated cuvette rotating about its vertical axis. They realized two variants of the experiments: "one-color" and "two-color." In the former case the pumping and probing of the system were performed with the same radiation (457.9; 430; and 420 nm), while in the latter case radiation at 337 nm served as the pump, and radiation at 420 nm as the probe. Identical results were noted. From comparison of the spectra of the triplet and singlet states of the molecules, the conclusion was drawn of a certain leveling of the bond orders in the macrocycle in the  $S_0 \rightarrow T_1$  transition.

The carotenoids perform various functions, in particular, they carry out energy transfer. Here the determining role is played by isomerization of the molecules in the triplet state. In Ref. 41, at least four different isomers were identified by the method of time-resolved spectroscopy. This served as the basis for a hypothesis on the possible channels of occurrence of the processes.

The systems were prepared with a train of 337-nm pulses of a nitrogen laser, while probing was performed with the pulsed radiation of the second harmonic of a neodymium laser with the same repetition rate. A spectroscopic measuring apparatus was used that was fitted with a double monochromator with dispersion subtraction, working in combination with a simple monochromator. The image was focused on the screen of a brightness amplifier optically coupled with an optical multichannel analyzer (OMA) type receiver. From 500 to 300 pulses were summed, while the background in the absence of the probe beam was subtracted. A strobe technique was used. The solutions of the substances were pumped through. The triplet levels were populated with the aid of a sensitizer, which consisted of an addition of anthracene.

The study of the structural dynamics of a solution of carbomonoxyhemoglobin subjected to photolysis is of great interest from the experimental standpoint.<sup>42</sup> This was achieved with a dye laser pumped with the radiation of a nitrogen laser in the 419-nm region. Resonance spontaneous Raman spectra were excited with the second anti-Stokes component of the stimulated Raman scattering of compressed hydrogen (218 nm). In turn the stimulated Raman scattering was excited with the fourth harmonic of a YAG:Nd<sup>3+</sup> laser. The authors were able to determine the region of time lags of the probe radiation corresponding to the essential smooth variations in the character of the spectra. This enabled them to make plausible hypotheses on the photochemical processes occurring in the system.

By using the technique of picosecond pumping and probing with a train of pulses with Q-switching and mode synchronization, the authors of Ref. 43 conducted a new study of the  $S_1$  and  $T_1$  states of molecules of all-trans-substituted carotene—an important biological substance. We note that carotene itself had earlier been studied repeatedly by time-resolved spontaneous Raman spectroscopy under conditions of photolysis and radiolysis.<sup>44</sup>

In the context of the general problem of the course of polymerization of a material, a model substance might be stilbene molecules, where this process occurs via the double bond C—C. This is allied with the problem of cis-trans conversions. To identify the intermediate short-lived structures as well as the character of the photolysis itself, very important information has been furnished by the method of time-resolved resonance spontaneous Raman spectroscopy. In particular, the authors of Ref. 45 were able to obtain the spectra of the cis- and trans-isomers of the triplet molecules. By comparing with the experimental and theoretical data known from the prior literature, they concluded that the molecules of stilbene in this state have a planar (or almost planar) structure in the trans geometry.

The methyl radical constitutes a very important product of explosive action, and also is a reaction center of processes of photodissociation of molecules. This fully justifies the attention paid to it by the authors of Ref. 46. They first obtained the resonance spontaneous Raman spectrum of this compound, including the totally symmetric stretching mode and its first overtone, and also the first overtone of the bending mode. In particular, they determined the mechanical anharmonicity coefficients. The photolysis was performed by irradiating with the third harmonic of a YAG:Nd<sup>3+</sup> laser. By using it also a dye laser was pumped, whose radiation in the region 640–650 nm was frequency-doubled and mixed with its fundamental harmonic. Thus a probe radiation was formed with smooth tuning about 215 nm, which enabled selective, resonance excitation specifically of the methyl radicals. The source substances were gaseous CH<sub>3</sub>I, CD<sub>3</sub>I, and CH<sub>3</sub>Br in an argon jet.

The process of photoreduction of benzophenone and its derivatives is considered typical of the course of photochemical reactions. To reveal the unclear details of transformations occurring in systems of this type, the authors of Ref. 47 applied the method of dynamic spectroscopy with a probe signal of resonance spontaneous Raman scattering. The concrete objects were 4-phenylbenzophenone and four of its deuterated derivatives. All the substances were dissolved in hexane, and besides, the first one in acetonitrile, where the photochemical processes occur in a way known to differ. Correspondingly, in the latter case, the lines of the cation radicals were also observed in addition to the lines of the triplet molecules. It was shown that the conversion of the molecules to the triplet state is not accompanied by a change in the structure of the phenyl rings and the character of the CO bond. Conversely, depending on the conditions of excitation, substantial changes were noted in the diphenyl group. The conclusion was drawn on the whole that such properties as the lifetime of the  $T_1$  level, the photochemical activity of triplet molecules, etc., are mainly determined by the "diphenyl + CO" fragment, which agrees also with the behavior of the spontaneous Raman spectra of the intermediate products of conversion of related compounds.

In Ref. 48, which was devoted to studying stimulated pulse radiolysis of the oxidation reaction of p-aminophenol molecules in alkaline aqueous solutions, preliminary resonance spontaneous Raman spectra of an unstable compound absorbing in the region of 440 nm were obtained. The authors ascribed it to the p-aminophenoxyl radical. In its structure the latter sharply differs from the radicals of other compounds substituted in the p-position having the symmetry  $C_{2\nu}$ , but is analogous to the anion radical of p-benzosemiquinone  $(D_{2h})$ , for which the spectrum of the protonated form has not been described in the literature. Since protonation can occur not only on oxygen, but also on the amino group, this question required elucidation.

In this situation in Ref. 49, the authors undertook a special study using the same method of time-resolved resonance spontaneous Raman spectroscopy. Pulse radiolysis served to stimulate the transformations in the system. The acidity and basicity of the solutions were varied over a broad range. Here it was established that, when pH < 2, the cation radicals of p-aminophenol are formed, as can be decided from the intensities of the lines of the stretching vibration of the CO group, as well as the lines of the phenol ring. Conversely, in alkaline solutions, when the absorption spectrum is slightly shifted toward the red, the p-aminophenoxyl radical is revealed. Also the great resemblance of the spontaneous

Very often complex organic compounds containing chromophores luminesce. This creates difficulties in detecting resonance spontaneous Raman scattering signals. Sometimes the luminescence can be suppressed by adding a quenching agent to the solution. But this method is not universal and is not theoretically correct. In many cases in the pulsed excitation of spectra, it is preferable to use time discrimination of the luminescent radiation based on the fact that the transitions in spontaneous Raman scattering occur practically instantaneously. Also a method has proved adequate to the problem in which one combines the technique of strobing the receiver with difference spontaneous Raman spectroscopy.<sup>50</sup> This was demonstrated in Ref. 51 with the example of dynamical measurements of a strongly luminescent substance—pyrene in solution. It is also interesting that the authors of the latter study were first to apply an XeCl excimer laser as the master laser. The combination of the technical means that were used enabled performing studies of pyrene molecules in  $S_0$ ,  $S_1$ , and  $T_1$  states.

In closing this section we shall show with the example of one substance—p-terphenyl in liquid solution—that spontaneous Raman spectra in the band of induced absorption of triplet molecules can very substantially differ, depending on whether the pumping of the system is performed by radiolysis or by photoexcitation.

Triplet states prepared by radiolysis were also studied in 1978 by the authors of one of the ground-breaking studies on this theme, where five lines were discovered.<sup>52</sup> However, the spectrum of the same compound proved to be considerably richer when subjected to radiolysis in vitrified matrices at T = 77 K, containing the same set of lines (except one) as those observed in Ref. 52, and a number of new lines.<sup>53</sup> Control experiments, as well as comparison with the spectrum of the molecules in the ground singlet state, led the authors of Ref. 53 to conclude that varied intermediate products are revealed in the two studies.

As is known, pulsed radiolysis in its physical essence is a nonselective method of pumping a system. In particular, by using electron impact, molecules of the solvent are ionized,



FIG. 1. Resonance Raman spectra of santaxanthin molecules.  $a-S_0$  state.  $b-T_1$  state. The latter is realized by using pulse photolysis.<sup>44</sup>



FIG. 2. Resonance Raman spectrum of the p-aminophenoxyl radical formed by radiolysis of a solution of p-aminophenol.<sup>48</sup>

whereby the subsequent course of the chemical conversions is predetermined to a considerable extent. As regards the concrete compound, p-terphenyl, it generally exhibits a strange behavior consisting in a practically complete identity of the spontaneous Raman spectra of the mono- and dianions of its molecules, which can be associated with the very high rate of discharge of the latter. It is also interesting that the infrared absorption spectra of both anionic forms are completely non-similar to one another.<sup>2)</sup> While it is yet difficult to give a noncontradictory explanation of the listed facts, it is still clear that they must be taken into account also in other situations when systems under study are subjected to radiolysis.

For the sake of illustration, Figs. 1–3 show the characteristic spectra of resonance spontaneous Raman scattering obtained in experiments studying the dynamical behavior of various systems.

### 2.2. Resonance stimulated Raman scattering: molecules in the first singlet excited state

In the excitation of complex saturable organic dyes in high-power resonance laser fields, one often observes in the secondary-emission spectra more or less narrow emission and absorption lines, distinguished by their peculiar properties, on the background of broad simulated luminescence (or near it). This effect was first discovered in solid frozen matrices of cryptocyanine in solution.<sup>54</sup> In subsequent years analogous experiments were performed with a number of different dyes, not only in such matrices, but also in liquid solutions at room temperature,<sup>55-62</sup> thus showing the universality of the effect. Thus rather extensive material has been accumulated up to now in this field, including also several theoretical studies. A number of reviews have been devoted to a rather detailed discussion of it.<sup>63-67</sup>

In the context of our problem, we are primarily interested in the question of to what type of secondary emissionresonance stimulated Raman scattering or resonance stimulated luminescence-are the observed spectral lines to be ascribed. Even the first study<sup>54</sup> proposed that one is dealing with resonance stimulated Raman scattering occurring in the vibrational levels of the first excited singlet electronic state  $(S_1)$  in a nontrivial scheme with the lowest virtual level. Later the concept of resonance stimulated Raman scattering was substantiated in a number of new experiments and adopted by most authors. It has also been shown theoretically by taking account of the movement of populations that the scattering process generally occurs more efficiently in electronically excited molecules, although special cases can occur in which normal molecules act as the scattering centers. Criteria have been proposed that allow one to distinguish some centers from others.65

We can state on the basis of the presented material that the effect of resonance stimulated Raman scattering constitutes a new method of studying vibrational transitions in molecules converted to the first excited singlet state.

It makes sense to compare the methods of solving this problem in two situations, in which the probe signals are resonance stimulated and spontaneous Raman scattering. First of all we note that in the former case very powerful light pulses act on the substance being studied, whereby many nonlinear effects become appreciable that complicate the



FIG. 3. Resonance Raman spectra of p-terphenyl molecules.  $I \rightarrow S_0$  state,  $2 \rightarrow T_1$  state. The latter is realized by using a simplified photolysis technique.<sup>53</sup> The asterisks indicate the solvent lines.

overall spectral pattern and which rule out any quantitative estimates. Moreover, under such conditions one must deal with the breakdown of the specimen itself. Being in essence "single-color," the method of stimulated Raman scattering does not allow one to discriminate the possible signals from other intermediate structures, e.g., triplet molecules, ionic forms, etc. Further, the existence of luminescence not only does not hinder the detection of resonance stimulated Raman lines, but conversely, is a necessary condition for their appearance, since their intensity is predominantly determined by the interference between these two types of secondary emission.<sup>66</sup>

Thus it seems valid to consider that resonance stimulated Raman scattering supplements the method of time-resolved spectroscopy based on measuring the probe signal of resonance spontaneous Raman scattering.

Thus far the sources of excitation of resonance stimulated Raman spectra have been the standard ruby lasers with passive or electrooptical shutters, or more rarely YAG:Nd<sup>3+</sup> lasers, combination lasers with liquid active media (carbon disulfide, benzene, nitromethane, and nitrobenzene), as well as narrow-band, smoothly tunable dyesolution lasers. In some cases two-cascade amplification of ruby pulses has been used, increasing the peak power up to 100 MW. A number of experiments have been performed with longitudinal and transverse pumping which is essential for distinguishing the signals from normal and excited molecules. The identification of the scattering centers has been performed also by using different criteria. Studies are known in which the resonance stimulated Raman spectra were excited by pulses in the picosecond range.

To give a view of the quality of the experimental material, Figs. 4-6 present micrographs of a number of spectra.

#### 2.3. Resonance CARS: triplet and singlet excited molecules

As was noted above, one of the fundamental defects of the CARS method consists in the disturbance caused by the interference of the amplitudes of the signals  $\chi^{(3)R}$  and  $\chi^{(3)NR}$ , which acquires an especially great significance in studying liquid solutions of low concentrations and gas mixtures. Usually the contribution of  $\chi^{(3)NR}$  is suppressed by an appropriate choice of the polarization of the interacting light waves.<sup>11</sup> Yet this problem has been studied mainly in application to the case of degenerate CARS, when both the pump and probe waves of the system have the same frequency (the first term on the right-hand side  $\omega_{AS} = 2\omega_1 - \omega_S$ ). In the nondegenerate variant of the CARS process these waves dif-



FIG. 5. Regions of the resonance stimulated Raman spectra of triscyanine molecules dissolved and vitrified in alcohol at different concentrations.<sup>157</sup>

fer in frequency  $(2\omega_1 = \omega_2 + \omega_3)$ , which entails new possibilities of polarization experiments. This situation has been analyzed in detail in Ref. 68.

The difficulties of measuring the CARS signal from impurities involving the nonresonance susceptibility are eliminated to a considerable extent by resonance excitation (at a strong electronic transition) of the CARS spectrum. This is favored in certain situations by simultaneous minimization of various combinations of the resonance denominators of the corresponding expression.<sup>69</sup> Here the cross section of the process itself increases so sharply that very small contents of substances become accessible to study. For example, this has been demonstrated brilliantly in the case of  $\beta$ -carotene by the authors of Ref. 70, who were able to reduce its concentration to  $5 \times 10^{-7}$  M and to trace the course of the intensity of the lines upon scanning the pump over the absorption band, i.e., to measure the excitation profiles. The obtained results suggested that the method of resonance CARS is appropriate for the problems of studying short-



FIG. 4. Regions of the Raman spectra of cryptocyanine molecules. a— Resonance stimulated Raman scattering. b—Resonance spontaneous Raman scattering of the same dye pressed into a tablet.



FIG. 6. Region of the resonance stimulated Raman spectrum of rhodamine 6G molecules in a vitrified solution.<sup>55</sup>

lived compounds, and which other authors have not failed to use.<sup>71-78</sup>

One of the first of these studies<sup>77</sup> involved chrysene dissolved in, and then polymerized in methyl methacrylate. Its molecules absorb in different regions of the spectrum, and in particular, in the near ultraviolet. Upon pumping the specimen, one first observes stimulated absorption, which overlaps the interval ~450–620 nm, and which belongs to the singlet excited state, and 325 ns later—the band of triplet molecules with the main peak near 560 nm. The data obtained aided in a deliberate choice of the experimental conditions.

The S<sub>1</sub> level was populated by the radiation of the second harmonic of a ruby laser (wavelength 347 nm, power and pulse duration 5 MW and 15 ns, respectively). In addition, a broad-band dye laser was used, which generated radiation in the regions of 580 and 735–780 nm. The spectral instrument was a monochromator, and the receiver an OMA. By comparing the CARS spectra measured with and without the pump in the working material and the spontaneous Raman spectra of powdered chrysene, it was possible to reveal two lines of medium intensity, ascribed to singlet excited molecules.

The object of Ref. 73, which was provoked by a publication on resonance stimulated Raman scattering,<sup>55</sup> was to elucidate the question of whether the structure of molecules of the rhodamines excited to the S<sub>1</sub> state varies substantially as compared with the normal molecules. As a result of painstaking measurements performed under various resonance conditions, and also by comparison with the infrared and backscattering spectra of two rhodamines, the absence of appreciable structural alterations was shown.

The authors of a later study came to the same conclusion, in which, in addition to rhodamines 6G and B, another compound of this class was studied—sulforhodamine.<sup>75</sup>

A natural development of the results on the problem of identifying the scattering centers by using the method of resonance CARS has been the painstaking study of the contour of the spectral bands in the rhodamines.<sup>74</sup>

Most of the experiments in the studies cited above were performed with nanosecond time resolution. At the same time, this is sometimes insufficient, even in studying triplet states, not to speak of singlet excited states. The former problem has been faced in studying solutions of nickel octaethylporphyrin—containing a metal of the transition group of elements.<sup>77</sup> Upon applying picosecond technique and probing a liquid solution of this pigment, the authors of the latter study on resonance CARS spectra investigated the dynamics of decay of the triplet  $T_d$  state in nickel, which arises upon exciting its *d* electron. They established that the characteristic time of this process is approximately equal to 290 ps.

Reference 78 compared the results of studying the same substance by methods of resonance spontaneous and coherent scattering.

On the whole, the derivatives of the metalloporphyrins constitute a very interesting class of compounds since, first, they play an exceptional role in living nature. Thus, hemoglobin is the carrier of oxygen, thereby controlling respiration. The cytochromes carry out electron transport in bioprocesses. Photosynthesis is conducted in plants and bacteria with the participation of porphyrins. On the other hand, these pigments have been widely applied in medical practice as diagnostic means and as pharmaceuticals. Finally, they are often used as dyes. The set of cited circumstances makes the problem very topical of studying them from all sides by various methods, including resonance CARS spectra. A major contribution to this problem has been introduced by the cycle of studies performed by the Minsk group of scientists.<sup>76</sup> Taking into account the importance of the problem itself and the multilevel character of the approaches to solving it in Ref. 76, let us examine the obtained results with appropriate completeness.

Figure 7 shows the diagram of a scrupulously developed automated apparatus of multipurpose design, which allows one to record with nanosecond resolution the resonance spectra of the degenerate and nondegenerate variants of CARS and coherent Stokes light scattering (CSLS), to perform measurements of the excitation profiles of their lines, and also to determine the invariants of the Raman scattering tensor in liquids (Ref. 76; see also Ref. 79). Its parameters are specified in the caption.

Liquid solutions of four metal-octaethylporphyrins were studied. It was shown by varying the pump power how all the characteristics of the resonance CARS and CSLS spectra are changed under the influence of the redistribution of the molecules over the electronic states. This was correlated with transition to scattering by triplet or else singlet excited molecules. Calculations were widely used, and in combination with the experimental data they enabled, in particular, the spectral lines to be attributed to the symmetry types of the vibrations responsible for them. We shall illustrate what we have said above first with the example of nickel octaethylporphyrin, which has already been mentioned.

Figures 8–10 show the degenerate CARS spectra of this substance dissolved in tetrahydrofuran recorded under different excitation conditions.

We see that, as the pump power in the region of the weakly allowed  $Q_{0-0}$  band is increased, ever more intense additional lines appear in various regions of the spectrum with simultaneous relative weakening of the lines corresponding to minimal pumping, for which an appreciable population of the excited electronic state has not yet occurred. Since the original lines are the same in all parameters as in the resonance spontaneous Raman spectrum, one



FIG. 7. Optical scheme of a spectrometer designed to study CARS. 1— YAG:Nd<sup>3+</sup> dye laser, 2—amplifier, 3 and 4—second-harmonic generators, 5–12—dielectric mirrors, 13–17—lenses, 18—cuvette containing the active medium of the dye lasers, 19,20—Fabry-Perot interferometers, 21—telescope, 22—diffraction grating, 23 and 24—diaphragms, 25—cuvette, 26—interference filter, 27—MDR-23 monochromator, 28—FÉU-79 photomultiplier, 29—IA-256-6 analyzer, 30 and 31—dye lasers.<sup>79</sup>



FIG. 8. Resonance degenerate CARS spectrum of octaethylporphyrin molecules dissolved in tetrahydrofuran at a pump power  $\sim 10^6$  W/cm<sup>2</sup>. The asterisks indicate the solvent lines.<sup>76</sup>

draws the natural conclusion that the additional lines belong to some (singlet or triplet) excited state.

Relying on the results of the measurements in the variant of nondegenerate resonance CARS with suppression of the coherent background with a polarization technique, the invariants of the nonlinear susceptibility tensor  $\chi_{iikl}^{(3)}$  were determined for a number of the spectral lines of normal and excited molecules. The obtained data enabled identifying the symmetry types of the corresponding vibrations. As a result it was established that the non-totally symmetric modes are active in the spectra under the chosen experimental conditions, as well as modes allowed only for the antisymmetric component of the scattering tensor. An analysis of the problem resting on the vibronic theory of resonance spontaneous Raman scattering, which takes account of the ability of some non-totally symmetric vibrations to mix various electronic states,<sup>80</sup> and also many experimental studies, e.g., Ref. 81, lead to identical conclusions.

To determine the electronic state populated upon pumping with a rather intense resonance light field, the excitation profiles were measured of a number of spectral lines. It turned out that two maxima exist in the profiles of the additional lines: a long-wave maximum at  $\sim 565$  nm, and a

*Ip*, relative units *Ip*, relative units *Constant of the second seco* 

FIG. 9. The same as Fig. 8 at a pump power above 107 W/cm<sup>2,76</sup>



FIG. 10. The same as Fig. 8 at a pump power above 10<sup>8</sup> W/cm<sup>2</sup>.<sup>76</sup>

short-wave maximum displaced with respect to the former by the amount of the frequency of the vibration being studied. To judge by Ref. 82, the same pattern for the same substance is also observed in the picosecond absorption spectrum. This effect is attributed to the intercombination conversion  $S_0 \sim \rightarrow T_1$ , which occurs very rapidly, whereby, after excitation of the molecules in the channel  $S_0 \rightarrow S_1$ , they go over into the triplet subsystem of levels, and ultimately into the long-lived  $T_d$  state. The fact that the situation is exactly as stated above was confirmed by calculations based on the equations of balance with account taken of the lifetimes of the activated levels.

The other example pertains to zinc octaethylprophyrin.<sup>76</sup> Its difference from the Ni-substituted compound consists in the absence in the zinc atom of *d*-electrons and hence, of  $T_d$  states. Moreover, this pigment possesses a different set of kinetic parameters. In addition, its solution luminesces strongly, and this is associated with restricted possibilities of obtaining resonance spontaneous Raman spectra, which are necessary at the interpretation stage for comparison. The literature decribes only the spectrum of this compound excited in the Soret band, for which mainly the totally symmetric vibrations are active.

A study was conducted in Ref. 76 of resonance CARS in two of its modifications—degenerate and nondegenerate. The latter, as before, was used to determine the symmetry types of the allowed transitions. Since the incident radiation was in resonance with the weakly allowed band  $Q_{0-0}$ , the CARS spectrum exhibited non-totally symmetric vibrations, and also vibrations of the symmetry type  $A_{2g}$ , which are forbidden for the symmetric tensor  $\chi^{(3)}$ . Experiments with variation of the pump power also showed that in the limit almost all the molecules are converted to the  $T_1$  state, but they are still not revealed in scattering, since the band corresponding to the transition  $T_1 \rightarrow T_2$  lies outside the bounds of the sharp resonance. Also the lines of singlet excited molecules are absent, apparently owing to the insufficient population of the  $S_1$  level.

Thus the authors of Ref. 76 convincingly demonstrated the rich possibilities of joint scientific and experimental approaches to solving various aspects of the time-resolved spectroscopy of resonance CARS.

#### 3. ACTION OF EXPLOSIVE WAVES ON MATTER

The problem has two fundamentally different aspects----the study of specimens following a high-power shock load with the aim of revealing the residual structural changes in them,<sup>83-87</sup> and the far more difficult problem of studying the dynamics of the transformations on the real time scale, which is the topic of this section. In both cases the methods of vibrational spectroscopy using spontaneous Raman, stimulated Raman, and CARS probe signals have proved highly fruitful.

The solution of the second problem according to its nature requires single-pulse excitation of the spectra with sufficient spatial and temporal resolutions. Quantitatively they are fixed by the fact that for many materials the front of the explosive wave predominantly has an extent of less than 1  $\mu$ m, while its velocity of propagation amounts in order of magnitude to 5 km/h. Therefore, strictly speaking, the chosen spectral method that satisfies these conditions must enable space and time measurements at least within the limits of 0.2  $\mu$ m and 10 ps, respectively. However, the requirements are made even more severe when one takes account of certain specific circumstances, e.g., when one must conduct a study of the regions of the target that lie immediately behind the front of the wave.<sup>88</sup>

Most of the studies in this field pertain to liquids and single crystals.<sup>89-95</sup> However, in recent years great interest has been shown also in certain heterogeneous systems, such as pressed tablets of a number of explosive materials.<sup>96-97</sup> Here the goal is set of studying at the molecular level their reactivity and other properties in scientific and utilitarian respects.

There are two fundamental methods of obtaining very large shock pressures under laboratory conditions. In the first method one uses a high-power explosive to create a strong shock wave in the specimen itself, or accelerates a plate, which then strikes this specimen. In the second method the projectile acting on the specimen is accelerated with a one- or two-cascade gun based on a light gas or powder. This method is distinguished by many advantages, and in particular, it enables one to perform experiments in direct contact with the working material without risk to the operator in person and without damaging the entire complex of apparatus that generates the plane wave having the assigned, controllable parameters. One conveniently obtains reproducible shock pressures here up to  $\sim 10$  Mbar.<sup>98</sup> In the spectroscopic practice of studying the post-action of high-power dynamic loads, explosion of wires has also been used, in which the current of a very powerful battery of capacitors is passed through the wire.83-86

Let us preface the description of the concrete results on time-resolved Raman spectroscopy of shock-compressed specimens with some remarks. The point is that an event of this type is accompanied by a considerable local increase in the vibrational temperature of the material. In other words, the high vibrational levels in it become instantaneously populated. This can impede the interpretation of the spectra, but, on the other hand, it yields new, valuable scientific information on the properties of the potential surfaces. Moreover, an explosive wave is capable of breaking intra- and intermolecular bonds (similarly to pulse radiolysis) and even of ionizing mclecules. The formation of radicals in solid targets of a number of organic compounds following the front of an explosive wave has actually been observed by xray photoelectron spectroscopy.<sup>99</sup> Finally, the effects cited above can be accompanied by an appreciable shortening or else lengthening of all bonds. In the former case, if we are dealing with molecular-type crystals, we must consider that they can lose here some of their inherent spectroscopic properties based on the approximation of taking separate account of internal and external forces.

It is expedient to start the presentation of the existing experimental material and its interpretation with a very simple molecular compound—liquid nitrogen. Many studies have been devoted to investigating it in the liquid and solid phases by various methods; they have revealed a number of features whose nature has not yet been finally elucidated. In particular, the course of its electric conductivity as a function of the temperature and pressure has proved very interesting. In addition, nitrogen is an important component of chemical technology in the synthesis of many energy-rich materials. All this, taken as a whole, stresses the topical nature of the problem being discussed and ultimately can favor the choice of a correct physical model adequate to the obtained results.<sup>93,94</sup>

The main goal of the studies performed in the given field with application of CARS spectroscopy was the attempt to elucidate from the character and behavior of the vibrational lines the question of the extent to which the anomalies of the electric conductivity can be attributed to the dissociation of nitrogen molecules, and to estimate the upper bound of the vibrational relaxation of levels populated, as has been stated, by the strong local heating of the material. In the first study on this topic pressures were attained up to 34 GPa and temperatures up to 4400 K.<sup>93</sup> A subsequent study<sup>94</sup> was able to extend the stated range considerably.

The experimental setup was described by the authors in detail in Ref. 100. Here, however, we shall restrict the treatment to briefly characterizing it. A projectile fired with a two-stage light-gas gun dynamically compresses the specimen, which is placed in an apparatus that reflects the CARS signal. A description of the cryogenic part is given in Ref. 101. To solve the given problem, the apparatus was somewhat modified. In particular, the possibility was envisaged of reflecting the shock wave to amplify the effect on the specimen. A dye-solution laser was used for broad-band pumping, which enabled obtaining a continuum over a range greater than 600 cm<sup>-1</sup>. The probe radiation was narrowband radiation near 557 nm from another laser of the same type. A multichannel receiving and measuring system was used. Pressures, densities, and the temperature were measured by using the ordinary procedures for explosive research.

As a result of the studies performed by the authors of Refs. 93 and 94 under very severe conditions (up to 40.8 GPa and 5020 K—upon reflection of the explosive wave), the vibrational frequencies, the line width, and the susceptibilities  $\chi^{(3)}$  were measured for transitions from the ground state and a number of excited vibrational states (in some cases up to the sixth). In particular, it was found that, up to dynamic loads of about 17.5 GPa without reflection of the explosive wave, or 30 GPa with reflection, the frequencies increase monotonically, and with further increase in the loading they also begin to decline monotonically. The data on the intensities of the transitions and the line widths indi-



FIG. 11. Typical CARS spectra of nitrogen under shock compression of 18.8 (a) and 35.4 (b) GPa. The spectra are recorded with single and double exposures to the shock load.<sup>94</sup>

cate that thermal equilibrium is attained in less than 10 ns. It was shown that the width of the lines in shock exposure is proportional over a broad range to the temperature, and that with maximum loading the dephasing time of the vibrations decreases to approximately 1 ps. The effects of the frequency extremum are tentatively ascribed to the change in the character of the intermolecular forces or else to dissociation and ionization of the molecules, with which the loss of transparency by the specimens are also correlated.

Figure 11 allows one to evaluate the quality and information content of the spectra.

As is known, very much attention has been paid in the spectroscopic literature to studying water. Nevertheless (paradoxically!), its structure has not been established unambiguously up to now. A number of physical models have been proposed that explain at least partially many of its properties. In particular, the so-called superposition model has become widespread, which is based on the assumption of the coexistence in liquid water of two spectroscopically well distinguishable types of molecules. One of them corresponds to strong hydrogen bonds, which lead to the formation of clusters, and conversely, the other to weak hydrogen bonds, which allows one to treat these molecules as monomeric and similar to the constituents of the vapor phase of the substance.<sup>102</sup>

Since an explosive wave can actively affect the external and internal bonds, the authors of Ref. 91 applied this method for testing the cited model. The other problem consisted in an attempt to identify  $H_3O^+$  or else  $OH^-$  ions in shockcompressed specimens; the formation of these ions might explain the giant jump in electric conductivity upon varying the pressure and temperature as observed in a number of studies.

The probe signal was the spontaneous Raman scattering signal in the region of the weakly structured, very broad



FIG. 12. A region of the spontaneous Raman spectra of the band of the stretching vibration of the OH group of liquid water under different experimental conditions. *1*—original specimen at room temperature and atmospheric pressure, 2—shock-compressed specimen, 3—specimen under static pressure of 0.4 GPa at a temperature of 670 °C.<sup>89</sup>

band of the stretching vibrations of OH, while the spontaneous Raman spectrum itself was excited with the broad line (up to  $\sim 20$  cm<sup>-1</sup>) of the 248-nm line of a pulsed KrF laser. The explosive experiment was performed with an apparatus not much different from that briefly described above.

Figure 12 shows a region of the spontaneous Raman spectrum of shock-compressed water in comparison with the spectra of the original specimen and also of a specimen subjected to static pressure at a temperature of 640 °C. If we pay no attention to the shift of the principal maxima, we see that the spectra differ substantially from one another in the region of smaller vibrational frequencies, namely, in that the other spontaneous Raman band examined there, inherent in "unperturbed" water, is weakened or disappears entirely owing to the action of pressure on the specimen. This effect becomes especially striking after separating the entire complex band into Gaussian contours.

According to the model proposed in Ref. 102, the lowfrequency component pertains to the molecules which in water are associated by strong hydrogen bonding. Conversely, the high-frequency component is ascribed to "free" molecules. This means that the obtained results indicate a partial breakdown of the hydrogen bonds under the influence of the dynamic load. This shows rather convincingly the plausibility of the views developed in Ref. 102 on the structure of liquid water. However, we note also that the study that was performed did not enable one to establish any signs of the existence of OH anion-radicals or other ionic forms. Nevertheless it is not ruled out that they are still contained in water, but in very small amounts inadequate to the low sensitivity of the method of spontaneous Raman spectra.

The only study in which the action of an explosive wave was probed with stimulated Raman scattering was devoted to studying liquid benzene.<sup>89</sup> It was preceded by two publications on stimulated Mandel'shtam–Brillouin scattering under the same conditions in water and acetone.

A diagram of the apparatus used in Ref. 89 is shown in Fig. 13. The benzene was subjected to a dynamic pressure of 1.18-0.2 GPa, being heated here to about 200 °C. The shock exposure was achieved with a single-cascade gas gun. Singlepulse radiation of the second harmonic of a YAG:Nd<sup>3+</sup> crystal laser was used to generate stimulated Raman scattering. Observation was conducted in a "backward" geometry. The spectral instrument was a one-meter Czerny-Turner spectrograph. The signal was recorded photographically. For the sake of perspicuity the stimulated Raman spectrum



FIG. 13. Diagram of the experimental setup for observing the reverse signal of stimulated Raman scattering in shock-compressed benzene. *I*—projectile, 2—helium-neon laser, 3—photodiode, 4—focusing lenses, 5—target, 6—working specimen, 7—quartz window, 8—dielectric-coated mirrors, 9—time-lag system, *IO*—spectrograph, *II*—YAG:Nd + <sup>3</sup> crystal laser, *I2*—second-harmonic generator, *I3*—apparatus for spatial separation of harmonics, *I4*—flash lamp in the time-lag system, *I5*—apparatus for O-switching.<sup>89</sup>

of benzene was photographed at the same film location in the absence of a dynamic load.

In addition to the line of the totally symmetric ("breathing") vibration of the benzene ring (992 cm $^{-1}$ ), a new line of comparable intensity was found on the photograph that was obtained lying toward higher vibrational frequencies. Its spectral location proved to be critical to the magnitude of the load. Thus, on varying the latter from 0.6 to 1.2 GPa, its displacement was increased from  $\sim 4$  to  $\sim 9$  $cm^{-1}$ . According to the authors of Ref. 89, in the working pressure range benzene can remain liquid or transform to a crystalline phase (the so-called benzene-P). If the first variant of the interpretation is true, this means that, on reaching the critical loads in condensed benzene, the intermolecular bonds are broken. There is nothing remarkable in this statement, and it is correlated with the results discussed above of the study of liquid water. On the other hand, the second variant of the interpretation faces no special objections a priori. Moreover, it seems preferable, since one can understand on its basis the dependence of the shift on the magnitude of the loading. Actually, if under a powerful shock load the distance between molecules is appreciably reduced, then the crystal that is formed cannot be treated any longer as a molecular crystal in the strict sense, corresponding to which one can observe also some monotonic shifts of the frequency of its vibrational modes.

The fact of the shift of the spectral line being discussed has also been established in an earlier study in which the investigation was conducted over a broader range of conditions using CARS spectroscopy. Despite the appreciable shock broadening of the line at the intermediate load of 2.1 GPa, the spectrum distinctly exhibited an intense high-frequency component. The same is also observed in the spectrum of nitromethane, which was recorded in this study in the region  $\sim 920$  cm<sup>-1</sup> of the vibrations of the C–N bond at a load of 3.3 GPa. Further increase in the loads in both cases is accompanied by the appearance of a strong quasicontinuous background and a general complication of the spectra, which can be associated with decomposition of the mole-

493 Sov. Phys. Usp. 35 (6), June 1992

cules or with population of higher vibrational levels.<sup>92</sup>

Taking account of the known property of the process of ordinary stimulated Raman scattering, which as a rule involves the single most intense and narrow spontaneous Raman line, and develops toward generating its harmonics of various orders as the pump power is increased, some authors express doubt concerning the prospects of applying singlepulse stimulated Raman scattering in studies of short-lived products of explosive action on matter. We note in this regard that resonance stimulated Raman scattering is not marked by the stated defect; its spectrum includes a practically complete set of the allowed vibrations,<sup>65,66</sup> whereby the limitation being discussed is removed. At the same time, the experimental means of realizing resonances in stimulated Raman scattering are quite varied.

As we have already emphasized, the problem of studying explosives under real conditions seemed highly attractive, i.e., at the instant of action on them of a dynamic load, and using various methods of Raman spectroscopy for diagnosis. It was considered that such experiments can yield extremely valuable information on the inner mechanisms of the course of explosions at various stages of the process, and ultimately facilitate a deliberate choice of the most effective explosives.

We know of studies along this line performed by spontaneous Raman spectroscopy.<sup>96,97</sup> Pentaerythritol tetranitrate and 1,3,5-triamino-2,4,6-trinitrobenzene were studied in the form of pressed tablets. In addition, the spectra were obtained of a number of related compounds under ordinary conditions, also under single-pulse excitation. In the context of our review the second of the cited substances is of especial interest. The optical part of the apparatus applied in Ref. 96 enabled obtaining spectra with radiation of various wavelengths: 355 nm (third harmonic of a YAG:Nd<sup>3+</sup> laser), 683 nm, formed from the second harmonic of the same laser and stimulated Raman scattering from strongly compressed hydrogen, and also radiation at 448 and 530 nm generated by a dye pumped with an XeCl laser. In all experiments the receiver was an OMA. Discrimination of luminescence and other interference was performed by strobing with a strobe width of 100 ns.

Figure 14 shows a region of the spectrum of the material being studied, including the stretching vibration of the C-N



FIG. 14. Single-flash spontaneous Raman spectra in the region 1130–1200 cm<sup>-1</sup> from benzene symmetrically substituted with  $-NH_2$  and  $-NO_2$  groups. *I*—specimen not exposed to shock, 2–5—specimens with dynamic loads of 3.0, 5.5, above 7.0, and above 7.5 GPa, respectively. The arrow indicates the line of the totally symmetric vibration of the  $-NO_2$  group.<sup>97</sup>

bond and the totally symmetric vibration of the NO<sub>2</sub> group, as a function of the shock load, which was varied over the range from 3 to  $\sim 7.5$  GPa.<sup>97</sup> We see well that the band of the totally symmetric vibration of the NO<sub>2</sub> group splits into two components, while as the shock load is made more severe, their intensities not only become equal, but apparently are even reversed. The spacing between the components amounts to about 8 cm<sup>-1</sup> and remains constant. The authors of Ref. 97 explain the observed effect by the breaking of the internal and external hydrogen bonds inherent in this compound, which is correlated with the constancy of the frequency of the observed new line. The concrete mechanism of their breakage can be the instantaneous heating of the material.

Earlier the authors of Ref. 103 had found an externally very similar phenomenon, namely-the splitting of one line of the stimulated Raman spectra of related compounds-pnitroaniline and its substituted derivative (p-nitromonomethylaniline) with increasing power of the pump pulses. Splitting was not observed in the disubstituted derivative. The results were interpreted qualitatively within the framework of concepts of Fermi-type resonance, which, according to Ref. 104, can arise between two or several vibrations of the same order and symmetry. It was considered that a sufficiently strong electromagnetic field of a light wave can cause an appreciable Stark shift of the levels and induce mechanical anharmonicity of the vibrations themselves. However, it was later shown theoretically that resonance is impossible under these conditions, in any case when one takes account of only the cubic anharmonicity.<sup>105</sup> Therefore we shall try to treat the results obtained in Ref. 103 from a new standpoint resting on the interpretation of the other facts in Ref. 97.

As is known, the oxygen atoms of the nitro group and the hydrogen atoms of the amino group when close enough can form external hydrogen bonds. Further, we shall assume that the latter are broken under the action of the high-power light pulse. The probable mechanism of such a process will be made more precise below. If this is true, an analogous pattern, i.e., the redistribution of intensity between the splitting components (without appreciable change in the spacing between them), must also be observed in the spontaneous Raman spectra of the same substances depending on their



FIG. 15. Region of the spontaneous Raman spectrum of p-nitroaniline at two concentrations of the substance dissolved in dioxane—0.06 mol/L (a) and 1.5 mol/L (b). The asterisks indicate the solvent line.

dilution in liquid solutions. The first such experiments were performed as early as 1957<sup>106</sup> and were repeated recently by using photoelectric recording.<sup>3)</sup> The results obtained for p-nitroaniline are shown in Fig. 15.

We see a distinct confirmation of the hypothesis presented above. It turned out that, upon an accessible dilution of the solution (25-fold), the relative intensity of the narrower satellite increases, which we can naturally interpret as the line of the vibration of the unperturbed molecular groups. As regards p-dimethylnitroaniline, which cannot form a hydrogen bond, here one observes a certain structure on the side of lower vibrational frequencies that is sensitive to dilution of the solution. However, its nature is not clear.

Thus, on the whole we can state that the influence discovered earlier of a high-power electromagnetic field on stimulated Raman spectra<sup>103</sup> agrees well with the hydrogenbond model, although the model of a Fermi-type vibrational resonance is not fully ruled out, provided only that we take into account the fourth-order anharmonicity. Actually, in a number of cases it can be comparable in order of magnitude to the cubic anharmonicity.<sup>107</sup>

As regards the mechanism of breaking of hydrogen bonds in the situation of stimulated Raman scattering, we note the following. The so-called optohydraulic effect has already been established long ago, and consists in the phenomenon that, when a giant laser pulse acts on liquid or solid specimens, shock waves arise in them, especially powerful when these systems absorb light appreciably. The pioneer study in this important field is that of Prokhorov and his associates.<sup>108</sup> The review of Ref. 109 described various physical models responsible for this effect. We can assume that precisely such conditions are realized in the case of excitation of stimulated Raman scattering in polycrystalline p-nitroanilines. Here the high local temperature in the zone of the focal spot and the channel created by the acting pulse in the specimen, along with specific features of the shock wave. are the true causes of the breakdown of the hydrogen bonds.

Now let us focus attention on the purely methodological side of the matter. We see from the "single-flash" spontaneous Raman spectrum presented above that it is rather weak with a high noise level. Consequently, the problem is important of further refinement of the entire complex of measuring apparatus. One faces an analogous situation, in particular, in studying the steady-state spectra of very thin films by the method of spontaneous Raman scattering,<sup>110</sup> or of surface layers of single crystals and glasses,<sup>111</sup> etc. Modernization can deal with various aspects of this apparatus.

Since the topic in this section is the simultaneous recording of a more or less broad region of the spectrum, which involves the application of an OMA of some type, then to receive the extremely weak output signal, as usual, it is expedient to refrigerate the OMA photocathode. In line with the results of the authors of Refs. 112–114, one can attain by this method an increase in the sensitivity from one to two orders of magnitude (see also Ref. 110).

The effect is even more striking if one adopts as the receiving-amplifying system a combination of an OMA with a microchannel plate (MCP).

In schematic form, Fig. 16 shows the image amplification based on an MCP. The attachment amounts to a photocathode deposited on a fiber-optic face plate, near which a MCP lies with channels of diameters from 10 to 40  $\mu$ m, hav-



FIG. 16. Schematic view of an image amplifier based on a multichannel plate. *1*—incident light beam, *2*—photocathode, *3*—multichannel plate, *4*—luminescent screen, *5*—observer, *6*—input electron, *7*—secondary electrons, *8*—contacts.<sup>115</sup>

ing a resistive coating and attached on both sides to metallic electrodes. The side turned toward the photocathode is at a positive potential with respect to the latter. The close geometry of the photocathode and the MCP causes but little distortion of the image, which is visualized with a screen with a layer of luminophore. One can find a detailed description of a number of similar systems in Ref. 115.

Also other technical realizations of MCPs have been described. Thus, for example, the authors of Ref. 116 proposed and created a two-dimensional visualizing photon counter, which allows obtaining high  $(3 \times 10^7)$  and stable amplification of electrons, based on applying several (up to five) MCPs. Of course, an MCP can operate also in combination with a photomultiplier, when different regions of the spontaneous Raman spectrum are successively isolated in time by rotating the dispersive element of the spectrometer. This is just what the author of Ref. 110 did in studying very thin films of various materials by the spontaneous Raman method.

In the overall hierarchy of multichannel receivers, the so-called charge-coupled devices (CCDs) occupy a special place. They were developed as early as 1969 and have now been converted into a very important product of microelectronics, produced by the industry of many countries and perfected by now. The photocathode of these receivers amounts to a multielement semiconductor structure, while the measured quantity is the charge.<sup>115,117</sup>

Among the extremely valuable characteristics of the CCD are the practically zero noise level, the high quantum yield, which has a maximum near 600 nm, and the broad dynamic range. All these qualities of CCDs have stimulated their incorporation into spectroscopic practice. One of the first studies along this line was conducted in connection with problems of astronomy.<sup>118</sup> Its authors analyzed in detail the problem of optimizing the entire complex of apparatus attached to the CCD, and developed and created a Dewar vessel to refrigerate the CCD itself and the corresponding electronics, etc.

A number of publications have appeared in the literature on the application of this technology in spontaneous Raman scattering, e.g., to obtain high-quality spectra under red-light excitation of substances that strongly absorb radiation of shorter wavelengths, or show a stronger luminescence when acted on by it, which hinders or completely rules out the measurement of weak spontaneous Raman lines. Recently the proposal was advanced of the possibility and expedience of using a CCD in experiments on time-resolved single-pulse spontaneous Raman spectroscopy with all the advantages accruing from this.<sup>119</sup> However, there is as yet no information on the testing of this proposal.

## 4. RAMAN SPECTRA ON THE REAL-TIME SCALE (PICO- AND FEMTOSECOND RANGES)

### 4.1. Intrapulse stimulated Raman scattering: nonresonance case

All the examples given above illustrating the rich potential of dynamical Raman spectroscopy pertain to the study of nonequilibrium, short-lived structures and states, when the signals to be recorded are obtained and imaged in the traditional way, i.e., in frequency coordinates. However, the studies of the time evolution of Raman spectra are far from being less important, although not yet so widespread. In most cases the task is to measure the relaxation characteristics with pump and probe pulses whose duration is considerably greater than the period of the vibrational modes. When the converse condition is fulfilled the processes acquire qualitatively new features. In particular, the very effect of intrapulse stimulated Raman scattering becomes possible, which is the object of discussion in this section of the review.

As we have already emphasized, the relationship  $\tau < 2\pi/\omega$  is realized already in the picosecond range, depending on the frequency of the vibration under study. This is a situation of acoustic modes of the type of the components of Mandel'shtam–Brillouin scattering and also of intermolecular vibrations of the acoustic and optical branches. Many important studies have been conducted in the field, including crystalline, vitreous, and liquid media. Within the framework of the present review the author intends to concentrate major attention on the behavior of the optical modes having relatively low frequencies ( $\sim 300 \text{ cm}^{-1}$ ), which are accessible at the contemporary level of development of femtosecond laser technology. Moreover we note that all the situations cited above are described by the theory in the same way in principle.

We shall assume that the intrapulse stimulated Raman scattering is excited in a one-beam scheme. An analysis of the problem for the case of crossed pump beams leads to analogous final results, although in the author's view the two methods differ from one another in a number of secondary details. However, it is very important that the first of them has a decisive advantage of fundamental character, since it allows the separate observation of different effects, especially when the study is performed under resonance conditions, i.e., inside the intrinsic absorption band of the system.

The fundamental features and peculiarities of the process are described even in the classical approximation. Let an ultrashort pulse act on the material, while obeying the condition  $\tau < 2\pi/\omega$ . Then the optical electromagnetic field of this pulse initiates in it an instantaneous stimulating force, which ultimately leads to generating stimulated Raman scattering owing to electrostriction and to the appearance of coherent running vibrational waves, homogeneous in phase in the transverse directions, and modulating the dielectric permittivity of the medium. Therefore they scatter a probe pulse of the same duration applied to the material with a variable time lag.<sup>4</sup>) The fact that the pump pulse passes through the specimen in a finite time is of fundamentally important significance. This is the very reason why nonidentical phases of the coherent vibrational wave correspond to different cross sections in the direction of propagation of the pulse, since the front layer undergoes the action of the stimulating force earlier than, say, the back layer. Consequently, as the pulse penetrates into the medium, the phase varies, and as has been shown, linearly with distance.

Thus, depending on the magnitude of the time lag of the probe pulse, one can "feel" inside the vibrational waves their different phases from the nodes  $[Q(t') = 0 \text{ when } t_D = 0,$  $\tau/2$ ,  $\tau$ ,  $3\tau/2$ , etc.] to the antinodes  $[Q'(t) = \pm Q'_0]$  when  $t_{\rm D} = \tau/4$ ,  $3\tau/4$ ,  $\tau/4$ , etc.]. If these pulses are relatively weak, then for them the coherent vibrational motion being discussed is as though frozen, and they yield an instantaneous picture of the process. The theory developed in the first study<sup>120</sup> has proved quite suitable for describing the main features and laws of intrapulse stimulated Raman scattering. Thus, it has been used to reveal the indicatrix of the scattered radiation, and quantitative estimates have been made of a number of side effects-the amplitudes of the vibrations, the red shift of the pump caused by its depletion, the influence on the pump of powerful probe pulses, etc., and many of the known facts have been interpreted. Also a direct connection has been discovered of intrapulse stimulated Raman scattering with the superposition of close-lying coherent states. It has been possible on the basis of the graphic physical model proposed in Ref. 120 to formulate a number of fundamental problems from the spectroscopic standpoint and new applications in allied fields of science. The further efforts of the same group of authors have been directed toward extending and generalizing the original theory, in particular, toward establishing the detailed connections bwtween the time- and frequency-dependent approaches to the problem.<sup>121,122</sup>

The starting point of the theory<sup>120</sup> was the equations for ordinary stimulated Raman scattering written in classical form and including all the necessary characteristics of the mode being generated and of the electromagnetic field of the light wave and of the medium itself:<sup>123</sup>

$$\frac{\partial^2 Q}{\partial t^2} + 2\gamma \frac{\partial Q}{\partial t} + \omega_0^2 Q = \frac{1}{2} N \left( \frac{\partial \alpha}{\partial Q} \right)_0 : EE,$$

$$\nabla \times (\nabla \times E) - \frac{n^2}{c^2} \frac{\partial^2 E}{\partial t^2} = \frac{4\pi}{c^2} N \left( \frac{\partial \alpha}{\partial Q} \right)_0 : \frac{\partial^2}{\partial t^2} (QE).$$
(4.1)

Here  $\gamma$  and  $\omega_0$  are respectively the decay constant and the frequency of the chosen mode, N is a measure of the density of oscillators,  $\alpha$  is the polarizability tensor, E is the electromagnetic field intensity of the light wave, n is the refractive index of the medium, which is assumed isotropic for simplicity, c is the velocity of light, and Q is the vibrational coordinate. The medium is assumed to be transparent, which allows us to neglect dispersion, at least in the case of small vibrational frequencies. This predetermines the collinear geometry of the phase synchronization of the acting beams. One also uses the approximation of a fixed pump field. When the listed conditions are fulfilled, Eq. (4.1) is substantially simplified, being converted to the form

$$\frac{\partial^2 Q}{\partial t^2} + 2\gamma \frac{\partial Q}{\partial t} + \omega_0^2 Q = \frac{1}{2} N \alpha' E_{\rm L}^2, \tag{4.2}$$

$$\frac{\partial^2 E}{\partial z^2} - \frac{n^2}{c^2} \frac{\partial^2 E}{\partial t^2} = \frac{4\pi}{c^2} N \alpha' \frac{\partial^2}{\partial t^2} (Q E_{\rm L}), \qquad (4.3)$$

Here we have  $\alpha' = (\partial \alpha / \partial Q)_0$ . On the basis of these equations the authors of Ref. 120 were able to reconstruct a rather complete picture of the mechanics and electrooptics of the coherent vibrations generated in the process of intrapulse stimulated Raman scattering, and also to describe many properties of the working medium.

Without going into the details (which is not the theme of our review), we shall cite only the principal results of the study that was performed. First, the amplitude and phase behavior of the vibrational coordinate Q(z,t) as the incident pulse penetrated into the interior of the specimen in the direction of the z axis was established. In analytic form it can be written as

$$Q(z > 0, t > 0) = Q_0 \exp[-\gamma(t - zn/c)] \sin[\omega_0(t - zn/c)].$$

Here the zero-point amplitude  $Q_0$  of the vibration equals  $2\pi IN\alpha' e^{-\omega_0^2 \tau_L^{2/4}} \omega_0 nc$ , while the letter *I* denotes for brevity the expression  $ncA^2 \tau_L / 8\pi^{1/2}$ , the integral intensity of the pump pulse. The exponential  $e^{-\omega_0^L \tau_L^{1/4}}$  reflects the requirement that the duration of this pulse  $(\tau_L)$  is shorter than the period of the vibration. In the converse case the amplitude  $Q_0$  vanishes. This implies that the process of intrapulse stimulated Raman scattering is threshold-free and propagates in the forward direction, whereby one can observe it in the traditional frequency representation in the opposed beam.

Further, quite evidently the pump must become exhausted in the development of the process of intrapulse stimulated Raman scattering. This is reflected in a red shift of the pulse. According to the estimates of Ref. 120, for typical values of the calculation parameters, this shift is easily detectable. Whenever the probe pulses are rather powerful, one must also take account of their influence on the pump and on the medium itself. This depends to a decisive extent on which phase of the coherent vibrational wave they fall into. It was shown in Ref. 120 that the amplitude of the vibrations is increased by the aggregate action of the different pulses. Since the different modes exist in differing phase states with respect to the probe pulses, i.e., a given time lag of these pulses for a single mode can correspond, e.g., to an antinode, and for another, a node or else a counterphase, this in the general case increases the mode selectivity of the intrapulse stimulated Raman scattering method.

An extremely important place in the theory of Ref. 120 is taken by the conclusion that the course of the process of intrapulse stimulated Raman scattering is accompanied by interference of the coherent states. In the case being discussed of nonresonance intrapulse stimulated Raman scattering they are the zero and first excited vibrational levels of the ground electronic state.

Finally, it is important to note also a number of other features of intrapulse stimulated Raman scattering, if the spectra are excited in a single-pulse scheme. As the theory shows, in this case one can separately affect the different components of the dielectric susceptibility tensor, and consequently initiate, e.g., a Kerr effect in the specimen and measure it by using a polarization technique, as in studying RIKE. Moreover the cited variant of intrapulse stimulated Raman scattering enables one to excite also quantum beats of different natures at the edge of the transmission band of the material.

A specific feature of femtosecond stimulated Raman scattering in frequency coordinates consists in broad-band pumping. Experiments of this kind have been performed as applied to a different range in studying ordinary stimulated Raman scattering. For example, in studying the generation of stimulated Raman scattering in a resonator, the authors of Ref. 124 showed that its efficiency depends to a great extent on the relationship of the widths of the lines of the exciting radiation and of the spontaneous Raman scattering, whereas the contour itself of the stimulated Raman line remains narrow. Reference 125 was devoted to obtaining quantitative data in this field. Later<sup>126</sup> the same authors posed the question of whether the results will depend on the width of the exciting line becoming comparable to the frequency of the spontaneous Raman line (or other type of scattering) or even exceeding it, with which the principal condition for observing intrapulse stimulated Raman scattering was correlated. To realize such a situation in the nanosecond range of durations, experiments were performed with stimulated Mandel'shtam-Brillouin scattering in compressed gases. It was established that this does not entail any detectable effects.

Let us present several examples of studying intrapulse Raman scattering, which pertain primarily to measurements in a crossed-beam scheme.

Reference 23 reported results obtained by the latter method for a single crystal of  $\alpha$ -perylene in the temperature region 20-300 K for different orientations of its crystallographic axes. The authors assumed that this is the first study on optical intrapulse stimulated Raman scattering with femtosecond resolution. Per se the choice of object was dictated by the fact that  $\alpha$ -perylene plays an important role in the thermal activation of the process of excimer formation. The base source was a ring dye laser. The working pulses had a duration of 70 fs at a wavelength of 620 nm. After four-stage amplification the light beam was split into two exciting beams and one probe beam with energy 1 mJ. The angle between the exciting beams was 3°. A nonplanar geometry was used to attain phase synchronization of the probe beam. The curves were constructed from the points obtained by averaging five laser bursts in five scans for averaging the slow fluctuations in the system.

In various experimental conditions with respect to wave vectors and specimen orientation, it was possible to bring about pulsed pumping of two of its fundamental vibrations at frequencies 80 and 104 cm<sup>-1</sup> with intensities corresponding to their polarization characteristics, as well as their sum and difference combinations. The time course of specifically the latter vibration is of especial interest, since it leads to periodic approach of the electronically excited molecules of  $\alpha$ -perylene, which gives rise to excimer formation. It was assumed that the electronic excitation occurs by the mechanism of two-photon absorption. Measurements were performed of the dephasing of the vibrations as a function of the temperature of the specimen. The corresponding spectra are shown in Fig. 17.

A very important sphere of applications of intrapulse



FIG. 17. Intrapulse stimulated Raman spectra of a single crystal of  $\alpha$ -perylene at two temperatures, 298 K (a) and 18 K (b). Fundamental modes 80 and 104 cm<sup>-1</sup> and their sum and difference combinations.<sup>23</sup>

stimulated Raman spectroscopy is the study of nonequilibrium configurations of molecules undergoing non-totally symmetric stretching and bending vibrations. For illustration let us present the time-resolved spectrum of liquid dibromomethane, which was also recorded in a scheme of intersecting beams polarized in the V plane in the region of the bending vibrations of the bromine atoms at the frequency  $173 \text{ cm}^{-1}$  (Fig. 18). But little different is another spectrum belonging to the same material, but excited in a V-H geometry, in which the pump pulses are polarized in the V and H directions, the probe pulse in the V direction, and the signal in the H direction.<sup>127</sup>

The presented Figs. 18 and 19 distinctly show oscillation peaks of varying intensity, whose envelope rapidly declines in magnitude at the beginning of the process, with a tendency toward saturation at its end. As always in such situations, the distance between the peaks equals the period of the vibration being studied; this means that it unambiguously defines its frequency. The first peak corresponds to the instantaneous response of the electronic subsystem of the molecules to the nonresonance action of the pump pulse. The induced orientation of the molecules and deformation of the innermost mode are responsible for the trend of the envelope. The initial, rather sharp decrease in the amplitude of the peaks is not directly connected to the dephasing of the



FIG. 18. Intrapulse stimulated Raman spectrum of liquid dibromomethane in the region of the bending vibration at 173 cm<sup>-1</sup> obtained in an intersecting-beam scheme with V-H polarization.<sup>127</sup>



FIG. 19. The same with single-beam pumping with radiation of wavelength 615 nm. Polarization in the V plane. 1-620-nm probe pulse, 2-609-nm probe pulse. Both are polarized in the same plane.<sup>127</sup>

vibrations, but is rather a consequence of the orientational motions of the molecules: the vibrations are most efficiently pumped in those molecules aligned parallel to the vector of V-polarization of the exciting pulses. Since the probe pulses are also polarized in the same direction, they are better scattered under these conditions. The entire complex of questions that we have touched upon has been analyzed theoretically in Refs. 20, 127, and 128. However, we shall not dwell on this point.

The spectrum shown in Figs. 19 and 20 pertains to dibromomethane excited in a single-beam scheme. The approximately collinear pump and probe pulses are polarized in the V plane. In this case the latter is dispersed with a monochromator, whereby the possibility exists of observing the "red" and "blue" components near the master wavelength of 615 nm. Their nature is due to the previously noted feature of the action of the transmitted probe pulses on the coherent vibrational wave in the material caused by the pump, namely, the fact that these pulses are incident with a chosen time lag, either in phase with it or in counterphase. Consequently, they impart energy to the wave under study or they borrow it. Thus the obtained results fit well into the theoretical model of intrapulse stimulated Raman scattering constructed in the classical approximation by the authors of Ref. 120.

Besides dibromomethane, other liquid substances have been studied by the latter method: trichlorotoluene, t-butylbenzene, fluorobenzene, etc. (with bending vibrations at



FIG. 20. Overall diagram of an apparatus for studying resonance intrapulse stimulated Raman scattering and diagrams of four of its variants designed to measure different physical quantities. *1*—pulse from laser source, 2—dielectric mirrors, 3—pump, 4—probe radiation, 5—modulator, 6—working specimen, 7—compensator, 8—receivers. Variants a-d correspond to measurements of the induced dichroism and birefringence, and frequency and amplitude modulation, which is determined by the choice of  $\lambda / 2$  or  $\lambda / 4$  plates.<sup>131,132</sup>

188, 135, and 240 cm<sup>-1</sup>, respectively). Measurements of this type in the RIKE variant have been concerned with dibromomethane and certain other anisotropic molecules.<sup>127,129</sup>

Additional information of experimental and theoretical character is contained in Ref. 136.

### 4.2. Intrapulse stimulated Raman scattering: resonance case

One feature of the process being discussed consists in the fact that, owing to the absorption of high-power ultrashort pump pulses, the first upper electronic state becomes populated to some degree. This makes combination transitions realizable between its vibrational subsystem of levels. However, this introduces the necessity of identifying them, not a simple problem, which is directly associated with the relationship between the duration of the pulses and the relaxation characteristics of the concrete system. If, in addition, the broadened pulses overlap simultaneously at least a pair each of the working levels in the normal and the electronically excited states, then the intrapulse stimulated Raman spectrum must exhibit a superposition of quantum beats of both origins.

Further, general considerations imply that precisely under conditions of resonance there are chances of separate observation of quantum beats of differing physical nature. This situation made feasible an analysis of the problem of the influence of the time delay of the probe pulse on its characteristics, with the aim of carrying out adequate schemes of experiment. Two studies<sup>131,132</sup> have been devoted to this complex of problems.

As before, the analysis is based on the case of singlebeam excitation of the spectra. The ultrashort pulse incident on the system is written as  $E_0(t) \exp(i\omega_0 t)$ . We assume that its action excites in the system the vibrations  $\gamma$  and  $\gamma'$  of the normal state, and also the vibrations  $\beta$  and  $\beta'$  of the upper electronic state.<sup>5</sup> We adopt the method of density matrices in the first approximation, in which, as usual, their elements  $\rho_{\gamma\gamma'}$  and  $\rho_{\beta\beta'}$  for  $\gamma = \gamma'$  and  $\beta = \beta'$  describe the movement of populations, or when  $\gamma \neq \gamma'$  and  $\beta \neq \beta'$ , the excitation of Raman scattering. Here the vibrational coordinate  $Q_{\beta}$  of the upper electronic state or the vibrational coordinate  $Q_{\beta}$  of the upper electronic state can be written in the form

and

$$Q_{\beta}(t) \sim \sum_{\beta} \rho_{\beta,\beta+1} q_{\beta+1,\beta} + c.c.$$

 $Q_{\gamma}(t) \sim \sum_{\gamma} \rho_{\gamma,\gamma+1} q_{\gamma+1,\gamma} + c.c.$ 

respectively.

The complex character of the mutual influences of the pump and the medium, and also the reaction to this of the probe radiation, predetermine a number of effects subject to observation, and which require being taken into account and analyzed in detail. Actually, the electric field intensity of the probing light pulse applied to the medium after a very short time interval  $\tau$  and transmitted through the thickness l of the specimen having induced coherent vibrational waves, unavoidably proves to be modulated. In analytic form this process can be written as

(4.4)

$$E'_{0}(t-\tau, l) = E'_{0}(t-\tau)\exp(a(t) + i\psi(t))$$
$$= E'_{0}(t-\tau)\exp\left(-\frac{\Delta\Gamma(t)}{2}l + i\frac{2\pi}{\lambda}\Delta n(t)l\right), \quad (4.5)$$

Here  $\Delta\Gamma(t)$  and  $\Delta n(t)$  are respectively the time-dependent absorption coefficient and refractive index of the medium. In turn, the modulation of the latter quantities is given by the expressions

$$\Delta\Gamma(t) \sim \left(\frac{\partial\sigma_{\gamma}}{\partial q_{\gamma}}Q_{\gamma}(t) + \frac{\partial\sigma_{\beta}}{\partial q_{\beta}}Q_{\beta}(t)\right), \qquad (4.6)$$

$$\Delta n(t) \sim \frac{2\pi}{9n} (n^2 + 2)^2 \frac{\partial \alpha_{\gamma}}{\partial q_{\gamma}} Q_{\gamma}(t) + \frac{\partial \alpha_{\beta}}{\partial q_{\beta}} Q_{\beta}(t). \tag{4.7}$$

Here  $\sigma$  and  $\alpha$  are the molar absorption cross-section and the real component of the polarizability of the radiative state, respectively, as referred to the individual vibrational amplitude q. We can also expect a frequency modulation of the probe beam, which is approximately described as

$$\Delta\omega(t) \sim \frac{4\pi^2}{9\lambda n} (n^2 + 2)^2 l \left( \frac{\partial\alpha_{\gamma}}{\partial q_{\gamma}} \frac{\partial Q_{\gamma}(t)}{\partial t} + \frac{\partial\alpha_{\beta}}{\partial q_{\beta}} \frac{\partial Q_{\beta}(t)}{\partial t} \right), \qquad (4.8)$$

and its amplitude modulation  $\Delta f(t) = -\partial \alpha(t)/\partial t$ , which depends on the time lag

$$\Delta f(t) \sim l \left( \frac{\partial \alpha_{\gamma}}{\partial q_{\gamma}} \frac{\partial Q_{\gamma}(t)}{\partial t} + \frac{\partial \alpha_{\beta}}{\partial q_{\beta}} \frac{\partial Q_{\beta}(t)}{\partial t} \right).$$
(4.9)

To describe fully the resonance specifics of intrapulse stimulated Raman scattering, the authors of Refs. 131 and 132 went over to the second-order approximation and calculated the elements of the density matrix, including the decay constants. They made the simplifying assumption that the dephasing time T of the electronic subsystem is much shorter than the duration of the pulse and that a narrow distribution of the width of the vibrational levels around the value 1/T corresponds to each vibronic state. Under these conditions we have

$$\rho_{\gamma\gamma}^{(2)}(t) \propto -\frac{M_{\gamma\gamma'}}{\hbar^2} \left( \frac{\rho_{\gamma}^0}{i(\omega_0 - \omega_e) + (1/T)} + \frac{\rho_{\gamma'}^0}{-i(\omega_0 - \omega_e) + (1/T)} \right) \\ \times \int_0^\infty \exp\left[ -\left(i\omega_{\gamma\gamma'} \frac{1}{T_{\gamma\gamma'}}\right) t' \right] E_0^2(t - t') dt', \qquad (4.10)$$

Here  $T_{\gamma\gamma'}$  is the vibrational dephasing time, and  $\omega_e$  is the frequency of the electronic transition (for simplicity—its value at the maximum of the absorption band). Omitting the details, we note that important conclusions stem from the derived expressions for the density matrix. Namely, if the incident pulse  $E_0^2(t)$  contains strong Fourier components at the frequencies  $\omega_{\gamma\gamma'}$  and  $\omega_{\beta\beta}$ , of the vibrational modes, then only in this case does intrapulse stimulated Raman scattering arise, both in the ground state and in the upper electronic state. By approximating these expressions with a very simple model of a harmonic oscillator, the authors of Refs. 131 and 132 were also able to write in explicit form the functions  $Q_{\gamma}(t)$  and  $Q_{\beta}(t)$  of the probe signals, the analysis of which enabled them to reveal all the features of behavior of the

coherent vibrations as functions of the sharpness of the resonance.

The theoretical views that were developed served as the basis for creating four variants of the experiment shown in Fig. 20. Scheme a corresponds to measuring the rotation of the plane of polarization of the probe pulse, which gives a linear measure of the anisotropic saturation of the absorption, i.e., the dichroism induced by the pump. Here the signal  $S_{a}(\tau)$  varies as a function of the lag  $\tau$  as  $\Delta\Gamma_{\mu}(\tau) - \Delta\Gamma_{\mu}(\tau)^{*}c(\tau)$ , where \* means convolution with the correlation function, which has the form  $c(\tau) = \int E_0^2(\tau) E_0^2(t+\tau) dt$ . The indices || and 1 mean that  $\Delta\Gamma$  was measured with the corresponding polarizations of the exciting and the probe pulses. In another scheme (b) one uses a quarter-wave plate, which polarizes the probe pulse elliptically before it is spatially separated with the pump. Thus experimental conditions are realized for measuring RIKE  $[S_{\rm b}(\tau) \propto (\Delta n_{\parallel}(\tau) - \Delta n_{\perp}(\tau)^* c(\tau)]$ . The transformation from measuring the induced absorption  $S_a(\tau)$  to  $S_{\rm b}(\tau)$  is done by adjusting the Babinet compensator-coil. Finally, the two last schemes c and d allow one to measure the frequency and amplitude modulation of the probe pulse induced by the pump  $[S_c(\tau) \propto (\Delta \omega_{\parallel}(\tau) - \Delta \omega_{\perp}(\tau)^* c(\tau)]$ and  $[S_{d}(\tau) \propto (\Delta f_{\parallel}(\tau) - \Delta f_{\parallel}(\tau)^{*}c(\tau)].$ 

The aspects briefly sketched above of the rather complex process of resonance intrapulse stimulated Raman scattering have been studied in the cited papers with the example of an aqueous solution of malachite green. The frequency of the vibrational mode of this dye is close to  $220 \text{ cm}^{-1}$ . In the spectrum it is isolated, since the modes with smaller frequencies belong to the strongly damped torsional deformations, while the modes with higher frequencies do not fit into the broadened contour of the pump pulse, and therefore are not excited. Pulses of duration 50--60 fs at a wavelength of 625 nm were applied for pumping, in resonance with the absorption band of the dye. The latter situation makes possible conditions of experiment adequate to the theory that was developed. The solution was impelled through and studied in the form of a jet 160- $\mu$ m thick. The energy of the exciting pulse was 0.2 nJ. A small part of it was aligned at a small angle with the latter in the medium and performed here the function of the probe of the system.

Thus the theory proposed by the authors of Refs. 131 and 132 and the experiments that they performed enabled them to discover the nature of the effect of intrapulse stimulated Raman scattering, including its resonance variant. This is of extremely great significance in understanding all the accompanying processes, in particular, the elementary event of light absorption itself. Here they showed that an unequivocal interpretation of the quantum beats, i.e., ascribing them to concrete physical characteristics of the material, which are altered upon exciting intrapulse resonance stimulated Raman scattering, is possible only in a single-beam experimental scheme. The apparatus was developed in four embodiments, based on a polarization methodology of recording the output signals, and distinguished by high sensitivity and linear response. By using this apparatus the phase, amplitude, and frequency modulation of the signals were observed separately for the first time-new effects predicted by the theory, and expanding and deepening our view of the physics of the process being discussed. It was established that one of the principal influences of the resonance conditions of excitation consists in ensuring the coexistence of absorption and dispersion processes. It was also revealed that at resonance the behavior of the initiated coherent vibrations is no longer described by a simple classical model, since the scattering cross section enters into a complex expression. In the general case in intrapulse stimulated Raman scattering vibrations are involved that correspond to transitions in electronically excited molecules or crystals. Criteria are given that enable one to distinguish them from transitions occurring in the normal state of these systems. As a result unique possibilities are created for studying the relaxation characteristics simultaneously in both situations.

Thus the authors of Refs. 131 and 132 "build a bridge" between the correct studies of intrapulse stimulated Raman scattering and the results on quantum beats that had previously been discovered and described in Refs. 14–18 by using the methods of excitation of spectra in a scheme of crossed beams and recording by an optical-correlation scheme. This is a highly essential forward step along the pathway of development of time-resolved spectroscopy of vibrational and electronic transitions in complicated molecular systems.

All the results described above, as well as those in the previous section of the review, pertain to the case in which the intrapulse stimulated Raman spectra are excited with one or two femtosecond radiation pulses. This fact is associated with certain demands on the power of such pulses: it must suffice for obtaining appreciable output signals, but not be so great as to exceed the threshold for breakdown of the specimen. Therefore (and for reasons of fundamental importance), the idea arose of pumping the system with a very long train of considerably less powerful pulses. Formally an analogous dilemma was discussed earlier in studies of hyper-Raman scattering.<sup>133</sup>

Recently this problem was solved successfully, and some advantages of this method illustrated with the example of  $\alpha$ -perylene in Ref. 134. Without touching as yet on the scientific ideology on which the interpretation of the results obtained in Ref. 134 rests, let us turn to the technological side of the matter.

The apparatus that was created was based on a new method of shaping very long sequences of ultrashort pulses with strictly fixed and stable characteristics (in the terminology adopted in the English language-the Pulse-Shaping Method), based on the Fourier relationships between the time-dependent and spectral properties of these pulses. To realize it, one needs a three-stage process: spectral decomposition of the pulse, i.e., obtaining its components separated in space, transformation of the spectrum, i.e., altering the relative magnitudes of the latter by using amplitude or phase filters, and finally, recombination of the spectrum, a process inverse to the first one. Ultimately a pulse is formed with a new time-dependent form. Special masks serve as the filters. If they are made in the form of a "comb," then one will obtain at the output a train of pulses with an interval between the components of  $\Delta t \sim 1/\Delta \omega$ , where  $\Delta \omega$  is the spectral period of modulation in the second stage of the process.

The experiments performed in Ref. 134 are based on using a geometry of two intersecting beams of a long train of ultrashort pulses, the interval between which was tuned to one of the vibrational modes—80 or else  $104 \text{ cm}^{-1}$ . To ob-

tain such a train, a femtosecond single pulse was transmitted through an optical system consisting of two diffraction gratings, two lenses, and a comb mask, whose functions, character, and sequence of action were described above.

The selectivity of amplification of the chosen mode was convincingly demonstrated. The authors of Ref. 134 interpreted the effect by using a very simple model of a pumped swing, i.e., a more or less sharp increase in the amplitude of a classical oscillator when excited "in rhythm". However, this conclusion was correctly disputed in Refs. 135 and 136 on the basis that the extension of classical concepts on the energy characteristics of a system is not correct, especially in the region of high excitations. A rigorous analysis of the problem is compatible with the viewpoint that the considerable increase in the mode selectivity involves the movement of the population of the first excited vibrational level rather than an increase in the energy of the individual oscillators. In other words, the question consists in the growth of the macroscopic polarization of the medium, rather than the energy properties and behavior of the individual molecules.135,136

However, in this problem we must not lose sight of the following circumstances. The argumentation of the authors of Refs. 135 and 136 is based on the assumption that the energy of the single pulse equals the total energy of the train. Yet if the latter is considerably greater, then the nuclear motions can be pumped more strongly in the absence of breakdown of the specimen. Moreover, important correctives to the theory are introduced by the resonance conditions of excitation of intrapulse stimulated Raman scattering, to which attention was paid in Refs. 135 and 136. Therefore the preparation of oscillators of high amplitude by using the intrapulse stimulated Raman scattering process is not at all a hopeless problem.

# 4.3. Prediction of the pathways of development of intrapulse stimulated Raman spectroscopy. Possible spheres of new applications

As is known, the key role in solid-state physics and molecular spectroscopy is played by phonon-phonon and electron-phonon interactions in the ground and excited electronic states of the system. Essentially, precisely the existence of the latter determines the very possibility of appearance of the process of Raman scattering in its different variants. On the other hand, the magnitude of these interactions is determined by the natural and induced anharmonicity of the vibrations, whereby the problem arises of studying the direct and indirect influences of this type in various conceivable situations.

In the spectroscopy of complicated compounds the representation in terms of characteristic vibrations is customary, which is valid in the case in which some particular functional group sharply differs from the skeleton of the molecule in its dynamical and kinematical parameters. Such, for example, are the -OH and  $-NO_2$  groups, the -C=-C-bond, aromatic and other rings, etc. Usually in such cases the interpretation of the vibrations is conducted on the basis of local symmetry. Yet the interaction of vibrations with large induced amplitude can destroy their characteristic nature, which entails a change in the symmetry group, and concomitantly an apparent breakdown of the selection rules.

In particular, the problem of removal of degeneracy belongs here, which is characteristic of small vibrations of certain polyatomic groups. This phenomenon was first observed in Ref. 137 in studying stimulated Raman scattering in the solution of a complex dye-triscyanine, which was excited with a very powerful light pulse from a ruby laser. It turned out that, depending on the concentration of the substance, the stimulated Raman spectrum in the region around 600 cm<sup>-1</sup> strongly varies. Namely, in the most concentrated solutions one observes one line (606  $\text{cm}^{-1}$ ), while as the solutions are diluted a systematically enhanced new line appears (601 cm<sup>-1</sup>), while the former line is simultaneously weakened down to total disappearance (see Fig. 5). In this region one finds doubly degenerate vibrations of the benzene rings contained in the structure of the dye. The natural assumption was made that under the action of large amplitudes it splits into two components with symmetries  $A_1$  and  $\mathbf{B}_1$ ; according to the vibronic theory of scattering they must be sensitive in different ways to resonance with the absorption (generation) band, which is shifted as a function of the concentration.

The potentialities of such experiments will increase incomparably if one applies the method of resonance intrapulse stimulated Raman scattering with multipulse pumping. Moreover, it is easily extended to the case of simpler molecules, since the existing femtosecond lasers open up a very broad spectral range.

Attention had been called earlier to the possibility in principle of controlling Fermi-type resonances by inducing anharmonicity. There is no doubt that the set of such problems can be extended by pumping the system with a long train of ultrashort pulses. Bearing in mind the great successes in creating lasers that generate pulses of durations down to 10–15 fs, we can count on covering the entire range of skeletal vibrations of molecules.

An especial place in the spectroscopy of molecules and solids is occupied by the so-called Jahn–Teller effect. It is observed in the presence of degenerate electronic states in nonlinear molecules and consists in the removal of this degeneracy by certain non-totally symmetric displacements of the nuclei. According to a theorem of these same authors, in a nonlinear molecule there is always at least one non-totally symmetric coordinate having such properties. The new potential surfaces have minima that do not correspond to a symmetric position of the nuclei, and which lie ever farther from it as the electron–phonon interaction becomes greater.<sup>138</sup>

Being very interesting per se, and therefore fully meriting independent study by using the new technique, the Jahn– Teller effect is also distinctly manifested in resonance Raman spectroscopy. Namely—it activates the vibrations inherent only in the antisymmetric scattering tensor, and alters the degree of depolarization ( $\rho > 0.75$ ) of the spectral lines belonging to it (see, e.g., Refs. 139–142). Especially strong influences, extending also to nonresonance conditions of excitation of Raman scattering, are observed if the effect involves the normal (original) electronic state. Moreover, studies along this line are of applied importance, in particular, in connection with the problem of phase transformations in activated crystals.<sup>120</sup>

It is also interesting to trace the development in time of another process of interaction of electronic and vibrational motions under the influence of the deformational modes (Renner-Teller effect<sup>138</sup>).

The optical excitation of energy states by light pulses whose duration is shorter than the characteristic times of the system being studied is accompanied by very interesting phenomena, among which are the photon echo and self-induced transparency. One can understand and describe them by taking account of the processes of interference of the different states that arise when these latter amount to a linear superposition of other states. In this situation, a giant macroscopic oscillating dipole moment arises in the system due to the ordering of the phases of the quantum transitions in the ensemble of particles forming the system. Various schemes of realizing the effect are possible, which has been named the "Raman echo" when one uses stimulated Raman scattering signals.<sup>143</sup>

Just as in all the methods of time-resolved spectroscopy, to observe the "Raman echo" one applies two pulses to the system with a controllable delay: one prepares the coherent states, and the other probes the system. The determining role here is played by the character of the broadening of the echo signal. The authors of Ref. 23 consider the inverse problem to be important—to use a modified technique of exciting intrapulse stimulated Raman scattering adapted to the case of the effect being discussed to obtain important information on the parameters of the inhomogeneous and homogeneous broadening in the spectra of different systems. However, there are no reports yet in the literature on performed experiments.

One of the fundamental problems of modern spectroscopy continues to be the elucidation of the causes and mechanisms of blurring of bands in electronic-vibrational transitions in polyatomic molecules. According to the experimental studies<sup>144-148</sup> a contribution to this effect can be introduced by nonlinear interactions of the vibrational degrees of freedom, i.e., anharmonicity of their motions. A recent theoretical analysis confirmed and in essential details refined the hypothesis advanced earlier of a special role in this process of certain deformational and librational modes.<sup>149</sup> In connection with what we have said above and with the importance of the problem itself, it would be interesting to study time-resolved intrapulse stimulated Raman spectra in the region of the cited modes, and in particular, with multipulse excitation with induced anharmonicity.

The authors of Ref. 150 showed that the appearance of quantum beats at the edge of transmission bands can occur under the condition of breakdown of the adiabatic and Condon approximations. Time-resolved experiments can cast light on the course of the corresponding process.

Since the time that lasers were invented, the dream of chemists has been the idea of using them to initiate controlled reactions, say, localized in individual chemical bonds. Thus laser chemistry arose, based on multiphoton absorption of infrared radiation quanta. However, the great advances in this field do not eliminate the problem. The next important step can be taken on the path of development and perfection of the method of intrapulse stimulated Raman spectroscopy. In this regard we note the following.

Reference 134 expressed apprehension concerning the destructive action of pulses of femtosecond duration. In the opinion of the author of this review, this apprehension is exaggerated. In a series of studies on resonance stimulated

Raman scattering of giant single pulses in the nanosecond range (see, e.g., Ref. 137) it was shown with numerous examples that an excellent means of avoiding this difficulty is to freeze the solution in a vitrifying matrix. Here, although a shallow channel is formed in the specimen by evaporation and ablation of part of the material, during the course of the entire experiment the radiation is still scattered by the undamaged (fresh) surface of the specimen. General considerations also imply that the vapor phase cannot become the source of its own signal that can distort the useful and recordable signal. For understandable reasons, the conditions are even more favorable for ultrashort pulses with considerably smaller energy.

Thus resonance intrapulse stimulated Raman spectroscopy, including its variant with multipulse excitation, is suitable for the problems of laser chemistry.

While discussing the behavior of a material in the field of a high-power explosive wave, we focused attention on the requirement of fast action of the optical part of the apparatus, which is not yet fully satisfied and is restricted by the duration of the probe light pulse (units and tens of picoseconds). Serious chances of improving this important characteristic, and at the same time increasing the time and space resolution of the measurements at all stages of the experiment can apparently arise from pumping and probing the system by the technique of multipulse intrapulse stimulated Raman scattering with optimization of the parameters of the corresponding pulse train. These spectra can also prove useful in connection with real-time study of processes of synthesis (with huge dynamic loads on a multicomponent target) of new compounds that are not formed under ordinary conditions.151

Immediately after the discovery of the effect of hightemperature superconductivity (HTSC) in compounds of the type of cuprates,<sup>152,153</sup> experimental and theoretical studies began on its mechanisms (see, e.g., Ref. 154). Spectroscopic studies have also contributed toward this problem, in particular, in Raman scattering. The cited method was first applied by the authors of Ref. 155. Then a series of publications on this theme followed.

Among the set of mechanisms of HTSC in the literature, also some are discussed that take account of the role of the vibrational degrees of freedom of the material. Here we can provisionally classify them into two groups. It is assumed in the first group that a strong electron-phonon interaction arises from insufficient screening of the Coulomb forces in HTSC, for which a considerable ionic character of the bonds is characteristic. In the second mechanism, one takes into account the large anharmonicity of the phonons in a two-well potential, while assuming a modificational instability of the material. For the case of cuprates of the composition  $YBa_2Cu_3O_{6+x}$ , the latter is correlated with a transition of the crystals from the tetragonal to the orthorhombic system. Various approaches are found to the microscopical treatment of numerous facts, including those pertaining to the study of the vibrational spectra of HTSC. 156-167

Thus the problem of testing for the true mechanism of HTSC is rather complicated and as yet has not at all been solved.

Recently the first attempt was described to apply the method of resonance intrapulse stimulated Raman spectroscopy to the given problem.<sup>168</sup> The spectra were excited in a two-pulse scheme and were observed in the form of quantum beats at the edge of the transmission band of a film of a compound with the composition  $YBa_2Cu_3O_{6+x}$  (x < 0.4). By varying the concrete values of x it was possible to obtain a material with either semiconductor or superconductor properties. Here, in the former case, oscillations were distinctly detected with a period of 142 cm<sup>-1</sup> that belonged to vibrations of symmetry A<sub>1</sub>, active in spontaneous Raman scattering. When the material transformed to the superconductive state they disappeared from the intrapulse stimulated Raman spectrum. A similar pattern had previously been observed in single-pulse resonance intrapulse stimulated Raman spectra of single crystals, films of various thicknesses, and bismuth and antimony powders, which are known not to belong to the class of HTSCs.<sup>169</sup> Hence the only correct conclusion was drawn that the real reason for the disappearance of the line at  $142 \text{ cm}^{-1}$  from the resonance intrapulse stimulated Raman spectrum does not consist in the breakdown of any type of structures under the action of the pump, but in the breakdown of the selection rules under resonance conditions of excitation. This agrees well with the noted result of the theory that in resonance intrapulse stimulated Raman spectra the scattering cross section enters into a complex expression.<sup>131,132</sup> Therefore the further theoretical analysis of the given problem is important in the highest degree. In addition to the cited studies, such an analysis can be based, e.g., on the results obtained by the authors of Refs. 170 and 171.

It also seems to the author of this review that it would be extremely interesting to extend a variant of nonresonance intrapulse stimulated Raman scattering to the set of objects under discussion, where the breakdown of the selection rules is known to be ruled out. If at the same time the spectra are excited with a long train of pulses, this will enable tracing the development of the process upon inducing anharmonicity. One cannot also rule out *a priori* the appearance of a temperature jump in the HTSC at the instant of action of the pump.

It was found as early as 1974 that under the influence of collisions or in a broader sense—intermolecular interactions in an ensemble of particles of condensed systems—often new spectral bands are excited that are forbidden by the selection rules for isolated particles. This effect, completely analogous to that observed in crystals in high-power external electric fields, has been called induced Raman scattering as applied to light scattering.<sup>172</sup> It immediately attracted the attention of many investigators and stimulated a great number of publications (see, e.g., Ref. 173).

It is quite evident that induced Raman spectra bear new information on the character of the intermolecular forces, which in addition can be extracted from time-resolved measurements.

Application of the methods of time-resolved vibrational Raman spectroscopy can prove to be an invaluable aid in studying a number of macroscopic properties of matter at the molecular level. This includes the dynamics of phase transitions of first and second orders (in particular, the general problem of soft modes in crystals of different classes, including ferroelectrics), the character of the changes in a solid that arise near its melting point, various aspects of vitrification of and ceramic formation in materials, the behavior of the low-frequency acoustic vibrations in submicroscopic particles in the phase decomposition of glasses and in systems with a multitude of point defects, etc.

#### 5. CONCLUSION

Dynamic Raman spectroscopy constitutes a very important field in modern molecular and solid-state spectroscopy, which has continued until the present to develop vigorously, to become perfected, and to be enriched with new ideas of a fundamental nature and the technical means of embodying them. Among the latter, we must primarily include lasers in the pico- and femtosecond ranges, which generate sufficiently powerful single pulses and very long sequences of them, strictly and controllably ordered in their parameters, and covering the ultraviolet, visible, and near infrared regions of the spectrum.

All the methods of dynamical spectroscopy are based on a simple idea: one uses an appropriate light pulse to excite in a system some particular nonequilibrium state, which is probed (interrogated) with a second pulse delayed in time and, in the general case, having a different frequency. Here, in the case in which we are interested, one records the signals of the spontaneous or else the coherent Raman light scattering as realized in practically all the known variants.

The set of problems solvable by using dynamical Raman spectroscopy is unusually broad and varied. The object of study is the structure and certain features of short-lived compounds of the type of molecules that have been converted in some way to the first triplet or the singlet excited state, their ionic forms and other products of photolysis and radiolysis, and also the intermediate products of decay, or conversely, of synthesis, which are formed in the material, e.g., under the action on it of very powerful dynamic loads. In the latter case the lifetime of the products, which are the objects of study, is no longer determined by the internal properties of the electronic–vibrational transitions, but by the velocity of the front of the explosion wave. This fixes the requirements on the entire optics of the concrete scheme of the apparatus.

For all the importance of the fields sketched out above for studying the physicochemical behavior of matter from the spectroscopic standpoint, yet another problem takes the front stage, namely, direct measurements with sufficient time resolution of the relaxational characteristics of spectra, i.e., the rates of decay and dephasing of vibrational states. A specific feature of such experiments, which have been performed in a multitude of different variants, consists in the idea that the durations of the pump and probe pulses are inherent in them, which considerably exceed the period of the vibrational modes being studied.

If the converse condition is satisfied, qualitatively new features appear in the physics itself and in the course of the scattering process. In particular, an extremely interesting effect unavoidably arises—intrapulse stimulated Raman scattering, which is observable on the real time scale in the form of quantum beats at chosen frequencies, which yields with great accuracy a quantitative measure of the relaxation behavior of the vibrational modes. Already a great number of experimental studies have been published on this theme, covering crystalline, vitreous, and liquid media. Moreover, bases have already been created for theoretical representations of this effect that are suitable to describe it both in the region of transparency and of absorption by the substance, i.e., under conditions of its resonance excitation.

One can state without exaggerating that the study of intrapulse stimulated Raman scattering has already been converted into a mainline field of contemporary time-resolved spectroscopy. The prospects of its further development and the possibilities of varied applications in allied branches of science and technology are so rich that it is yet hard to survey them. Let us point out only the fields that seem to be the principal ones.

A large number of conceivable studies are linked by a direct or indirect connection with anharmonicity of vibrations—a very important characteristic of real systems. This includes, so to speak, a number of the inner problems of spectroscopy itself (selection rules, the Jahn–Teller effect, and expecially its manifestation in Raman scattering, blurring of absorption and luminescence bands in polyatomic molecules, etc.), as well as many extremely valuable, albeit special, problems, e.g., the creation of a new method of laser chemistry based on intrapulse stimulated Raman scattering, testing of the nature and mechanisms of high-temperature superconductivity, etc. In practically all situations the possibility of measured induction of anharmonicity is highly essential. In principle this can be attained by multipulse pumping.

The further development of the latter method urgently demands the invention of new laser sources to make studies over a broad spectral range accessible. A theoretical problem of first-rank importance is also the derivation of the selection rules for the resonance variant of intrapulse stimulated Raman scattering. It has already been noted in the literature that they differ from the usual ones, with which one can correlate the distinctive dependence of the intensity of these spectra on the spontaneous Raman cross section.

Time-resolved spectroscopy has great potential as a method of discovering on the molecular level the mechanisms of the course of many macroscopic processes in solids, such as phase transitions, melting, heat conduction, etc. Only the first steps have been taken in this interesting field.

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- <sup>1)</sup> To keep the phonetic resemblance of the Russian and foreign abbreviations, it is expedient to decipher the corresponding process as "resonansnyĭ indutsirovannyĭ kerr-éffekt"—RIKÉ (resonance-induced Kerr effect).
- <sup>2)</sup> Private communication from A. N. Sidorov.
- <sup>3)</sup> The author thanks M. Ya. Tsenter for performing the experiment.
- <sup>4)</sup> In a scheme of intersecting pump beams, owing to intrapulse stimulated Raman scattering, conversely, standing waves are formed in the material, which is reflected in a somewhat different description and details of the process itself.
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