

Nonlinear laser spectroscopy of gases, gas flows, and low-temperature plasmas

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The potentialities of gas analysis by the methods of active Raman spectroscopy based on coherent four-proton interaction of high-power laser beams with the resonance cubic nonlinearity are examined. Particular attention is paid to the possibility of measuring the parameters of gas discharges, flows, and flames, and also to the detection of low-level impurities in gases. A comparison is made with the traditional methods of spontaneous Raman spectroscopy. We show that the coherent methods of optical gas analysis possess a number of important advantages over the traditional methods, and show promise in many scientific and technical applications. The review is based on materials published in the scientific literature in the past two or three years, and on materials of domestic and international conferences on laser spectroscopy and gas diagnostics during recent years.

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INTRODUCTION

The progress in the technology of tunable-frequency lasers has created a basis for vigorous development of new nonlinear-optical methods of spectroscopy, which have recently found broad and energetically growing applications in many allied fields.¹⁻⁴ These methods have especially broad potentialities in practical gas analysis.

One of the most universal methods of nonlinear laser spectroscopy is coherent active Raman spectroscopy (CARS).^{2,3} (The most widespread variant of this method is also called coherent anti-Stokes light-scattering spectroscopy; the latter is equivalent to the English-language abbreviation CARS-coherent anti-Stokes Raman spectroscopy.)

This type of spectroscopy is closely related to spontaneous Raman spectroscopy, and has practically all its merits. However, it considerably surpasses spontaneous Raman spectroscopy in the level of the detectable optical signal, in spectral and spatial resolution, speed of action, in the considerably smaller level of optical noise and stray light, and in the richness and completeness of the spectral information that one can obtain with it on the material being studied, etc.

CARS is closely allied with other nonlinear methods

whose detailed development has occurred in the last several years that have passed since the writing of the review of Ref. 2. Above all, these include the methods of laser modulation spectroscopy: amplifications (attenuation) spectroscopy arising from stimulated (or inverse) Raman scattering-stimulated Raman gain (or loss) spectroscopy (SRGS or SRLS), and its various polarization and interference variants. They possess similar merits and substantially supplement CARS.

These and other coherent nonlinear-optical methods are highly promising for nonperturbing local monitoring of the composition, temperature, and pressure of gas mixtures, in probing excited and nonstationary gaseous media and aerodynamic flows, and in studying explosive and discharge processes in gases and plasmas, etc. Together with the method of spontaneous Raman scattering, these methods now constitute an extremely powerful and varied arsenal of laser methods for gas and plasma diagnostics that holds great applied potentialities.

Currently an extensive literature exists that is devoted to applications of CARS and related methods in gas analysis, and a considerable experimental material has been amassed on this topic that was not included in the view of Ref. 2.

In this review we attempt to systematize and generalize these studies, and also to compare the various coherent nonlinear-optical methods of gas analysis with one another and with the method of spontaneous Raman scattering. A brief sketch of the theory of coherent laser methods of gas analysis is given in Sec. 1 using the example of CARS. Section 2 discusses the features of the experimental realization of these methods. Sections 3-5 deal with the concrete potentialities of application of CARS to problems of gas analysis and with the most characteristic results. Section 6 briefly characterizes several new spectroscopic schemes that employ the methods of nonlinear optics. CARS is compared separately with other nonlinear-optical methods and with spontaneous Raman scattering (Sec. 7).

1. FUNDAMENTALS OF THE THEORY OF THE CARS METHOD

The essence of the CARS method² consists in the excitation and phasing in a large volume of a material of a selected Raman-active molecular vibration of frequency Ω by using two laser waves of frequencies ω_1 and ω_2 such that $\omega_1 - \omega_2 \approx \Omega$ (the phasing occurs in the region of overlap of the rays characterized by ω_1 and ω_2).¹⁾ A probe ray of frequency ω can be effectively scattered by molecular vibrations that have been excited and phased in this way into the Stokes or the anti-Stokes region. That is, a three-wave mixing process occurs: $\omega_{\sigma,a} = \omega \mp (\omega_1 - \omega_2)$ (it is often convenient to employ one of the pump waves as the probe wave). In CARS the spectroscopic information on the material is extracted by analyzing the variation of the amplitude (phase, polarization) of the component of the probe ray coherently scattered into the Stokes or anti-Stokes region as a function of the frequency difference of the pump waves $\omega_1 - \omega_2$ as one or both of the frequencies ω_1 and ω_2 are tuned (for more details, see Refs. 2 and 3).

Such four-photon processes in centrosymmetric media are described by the third-order nonlinear optical susceptibilities $\chi^{(3)}$, which are the coefficients of the expansion of the macroscopic polarization of the medium as a power series in the amplitudes of the electric field intensity of the corresponding light waves. For CARS this expansion for the polarization at the frequency of the coherently scattered wave $\omega_a = \omega + \omega_1 - \omega_2$ has the form^{2,3}

$$P(\omega_a) = \chi^{(1)}E^{(a)} + D\chi^{(3)}EE^{(1)}E^{(2)*} + \dots, \quad (1)$$

Here $\chi^{(3)}$ is the nonlinear optical susceptibility (a fourth-order tensor in the general case; see below). E and $E^{(1,2,a)}$ are the complex amplitudes of the waves at the frequencies ω , ω_1 , ω_2 , and ω_a , respectively. The numerical coefficient D allows for the existence of frequency degeneracy: $D=6$ if $\omega \neq \omega_1, \omega_2$, and $D=3$ if ω

$= \omega_1$ or $\omega = \omega_2$. Here the intensity of the new light wave at the frequency ω_a generated by the nonlinear component of the polarization in (1) can be represented by the following formula^{2,5}:

$$I_a = \left(\frac{4\pi^2\omega_a}{c^2} \right)^2 \frac{|D\chi^{(3)}|^2}{n_1 n_2 n_a} I_1 I_2 L^2 \left[\frac{\sin(\Delta k L/2)}{\Delta k L/2} \right]^2, \quad (2)$$

Here I , I_1 , and I_2 are the intensities of the pump and probe waves at the frequencies ω , ω_1 , and ω_2 (all considered to be plane waves), L is the length of the region of interaction of the waves, and $\Delta k = |\Delta k| = |k + k_1 - k_2 - k_a|$ is the wave detuning, where the $|k_i| = k_i = \omega_i n_i / c$ are the wave vectors of the waves at the frequencies ω_i ($i=1, 2, a$).

In condensed media we find $\Delta k \neq 0$ for collinear propagation of the waves, owing to the linear dispersion of the medium. However, in gases that are not too dense, where the dispersion of the refractive index is rather small, the pump waves can effectively interact even with collinear propagation, since in this case, as a rule, we have $\Delta k L \leq 1$ for $L \approx 10-100$ cm.⁶ Moreover, the employment of sharp focusing of the beams into a volume of length $b \leq 1_{\text{coh}} = \pi / \Delta k$ completely eliminates the problem of the need to match the phases of the collinear interacting beams (see below).

When the pump frequency difference $\omega_1 - \omega_2$ is tuned to the frequency of a selected molecular vibration, one can represent the nonlinear susceptibility $\chi^{(3)}$ in the absence of one- or two-photon absorption in the form

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

Here $\chi^{(3)R}$ is the resonance component of the susceptibility associated with the molecular resonance being studied, and $\chi^{(3)NR}$ is the nonresonance component associated with electronic transitions in the medium and with other nuclear transitions far from resonance. Upon employing the simple model of a harmonic oscillator, we can derive an expression for $\chi^{(3)R}$ in the following form:

$$\chi^{(3)R} = \frac{N_g - N_l}{2\omega_a^2 \hbar D} \frac{d\sigma}{d\Omega} \cdot \frac{\Omega c^4}{\Omega^2 - (\omega_1 - \omega_2)^2 - 2i\Gamma(\omega_1 - \omega_2)} \approx \bar{\chi}^{(3)R} \frac{\Gamma}{\Omega - (\omega_1 - \omega_2) - i\Gamma}; \quad (4)$$

Here

$$\bar{\chi}^{(3)R} = \frac{1}{D} \frac{N_g - N_l}{4\hbar^2} \frac{c^4}{\omega_a^2} \frac{d\sigma}{d\Omega} \quad (5)$$

is the "peak" value of the resonance cubic susceptibility at the center of the line, $d\sigma/d\Omega$ is the molecular Raman cross-section (in $\text{cm}^2/\text{steradian}$) from the vibrational-rotational transition at the frequency $\Omega = (E_l - E_g)/\hbar$, where $E_l(E_g)$ is the energy of the upper (lower) state of the transition being treated; $N_l - N_g$ is the difference between the equilibrium values of the number density of molecules in the lower and upper levels of the transition, and Γ is the homogeneous halfwidth of the molecular resonance (in radian/sec).²⁾

¹⁾ Actually, coherent excitation by the described method can occur for any transition in the medium under study (and not only for a vibrational transition). In particular, vibrational, vibrational-rotational, and pure rotational transitions can be excited with equal success in the molecules of a gas.

²⁾ In the presence of an inhomogeneous broadening of the transition being studied (e. g., Doppler broadening), we must in addition average Eq. (4) over the frequency distribution function of Ω .

We see from (4) that $|\chi^{\text{GR}}|$ has a maximum at $\omega_1 - \omega_2 = \Omega$. The relationship of the imaginary component of the susceptibility in (4) to the pump-frequency difference $\omega_1 - \omega_2$ coincides in form with the contour of the spontaneous Raman spectral line involving the selected transition.

However, the shape of the spectral line of the CARS signal differs from that of the spontaneous Raman line because, in accordance with (2), the coherent signal is proportional to the square of the modulus of the cubic susceptibility $\chi^{(3)}$ given by (3) and (4). Figure 1 shows the form of the CARS line calculated with (3) and (4) taken into account. Its characteristic features are the nondispersive pedestal involving χ^{GNR} ; as well as the presence of a maximum (near $\omega_1 - \omega_2 \approx \Omega$) and of a minimum shifted from Ω by an amount proportional to $\Gamma(\chi^{\text{GR}}/\chi^{\text{GNR}})$. This form of the spectrum enables one to calibrate the intensities of the different Raman lines in terms of the quantity χ^{GNR} by comparing the magnitude of the signal at the maximum of the spectrum with the nonresonance signal generated by the pedestal.

However, the relative magnitude of the pedestal is small in single-component gases of not very great density. For example, in nitrogen at $p = 1$ atm and $T \approx 300$ K, we have $\chi^{\text{GNR}}/\text{Max}|\chi^{\text{GR}}| \approx 0.05$. In pure H_2 for the individual J -components of the Q -band, this ratio is even smaller, etc. In these cases when the χ^{GR} line has a Lorentzian shape [see (4)], the square of the modulus of the total susceptibility $|\chi^{(3)}|^2$ near $\omega_1 - \omega_2 \approx \Omega$ coincides in form with the imaginary component of χ^{GR} ; i.e., with the shape of the spontaneous Raman line. However, in the case of inhomogeneous broadening of the Raman resonance, and in particular, in the presence of Doppler broadening of the shape of the CARS line, the square of the modulus of $\chi^{(3)}$ described by dispersion will not coincide with the shape of the spontaneous Raman line given by the dispersion of the imaginary component of $\chi^{(3)}$ (even in the absence of a pedestal associated with χ^{GNR}).⁷

In sufficiently dense gases the width of the molecular resonance is determined by the rate of collisions of molecules with one another. This increases with increasing density:

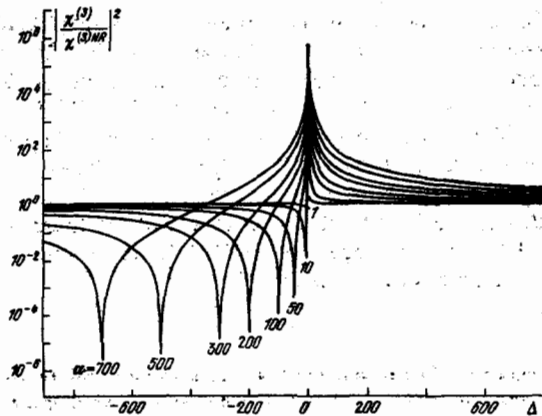


FIG. 1. Calculation of the shape of the CARS spectra for various values of $\alpha = \chi^{(3)\text{GR}}/\chi^{(3)\text{GNR}}$ and $\Delta = \Omega - (\omega_1 - \omega_2)$.

$$2\Gamma \approx 2\Gamma_0 + B\rho, \quad (6)$$

Here $\rho = N/N_0$ is the density of the gas in amagats (N_0 is the density of molecules in the gas under normal conditions, i.e., Avogadro's number), and $B = B(T)$ is a parameter that depends on the temperature. For example, at $T \approx 300$ K for the Q -band of the methane (CH_4) molecule, we have $2\Gamma_0/2\pi = 7.6$ GHz (the total width of the Q -band arising from J -splitting), and $B/2\pi = 0.35$ GHz/amagat. For the $Q_{01}(1)$ line of the hydrogen molecule (H_2), we find $2\Gamma_0/2\pi = 1.2$ GHz (Doppler broadening), and $B/2\pi = 0.051$ GHz/amagat.

Hence we see from (3) and (5) that the power of the CARS signal at the center of the line for sufficiently large N does not depend on the density, in contrast to the spontaneous Raman signal, which increases in proportion to N .

In order to get the maximum power of the recorded anti-Stokes signal, in CARS focusing of the interacting beams inside the studied volume of gas is employed. This increases the intensities I , I_1 , and I_2 for fixed values of the power of the beams P , P_1 , and P_2 . However, as we can easily see, unlimited increase in the degree of focusing of the pump waves will not lead to an unlimited increase in the total power of the signal being detected, owing to the contraction here of the length $L \approx l_{foc}$ of the region of effective interaction of the beams (l_{foc} is the length of the focal volume of the focused beams). As analysis shows,⁸ when $l_{foc} \leq (\Delta k)^{-1}$, l (where l is the length of the cuvette containing the gas), the total power of the anti-Stokes signal is stabilized at the following level, which is determined solely by the total powers of the pump beams and the parameters of the medium:

$$P_s = \int_0^l I_s(r) r^2 dr \approx \left(\frac{16\pi^4}{\lambda^3 c}\right)^2 |3\chi^{(3)}|^2 P_1^2 P_2; \quad (7)$$

Here the refractive index of the gas has been assumed to be unity, and the integration in (7) is performed over the entire cross-section of the beams (the pump beams are assumed to have a Gaussian intensity profile). Also we have $\lambda = 2\pi c/\omega$, where $\omega \approx \omega_1 \approx \omega_2 \approx \omega_0$. This formula is written for the most widespread CARS scheme in which $\omega_s = 2\omega_1 - \omega_2$.

Upon employing (4) and (5) and taking (6) into account, we can put the expression (7) into the following form when $\chi^{\text{GR}} \gg \chi^{\text{GNR}}$ (see also Ref. 9):

$$\frac{P_s}{P_1} = \frac{q_s}{q_1} = N_0^2 \left(\frac{\lambda}{2}\right)^4 \frac{(d\sigma/d\Omega)^2}{(\hbar c \Gamma_0)^2} P_1 \left[\frac{\rho}{1 + (B\rho/2\Gamma_0)} \right]^2; \quad (8)$$

Here $N_0 = 2.68 \times 10^{19} \text{ cm}^{-3}$ is Avogadro's number; the equilibrium occupancy of the excited states is ignored.

In (8) we have introduced the number of photons in the pulses of anti-Stokes (q_s) and probe (q_2) radiations.

It is important to stress that practically the entire power of the anti-Stokes signal given by Eqs. (7) and (8) is generated within the limits of the focal "spot" of the lens having a volume $V \approx 1.35 l_{foc}^2 \lambda$, where $l_{foc} = b = 2\pi w_0^2/\lambda$ is the confocal parameter of the focused Gaussian beams, and w_0 is the radius of the beams at the $1/e^2$ level in intensity. In the limiting case of "stiff"

focusing, we have $w_0 \approx \lambda$ and $V \approx 50\lambda^3$. If radiation of wavelength $\lambda \approx 500$ nm is employed, then we have $V \approx 0.85 \times 10^{-11}$ cm³. Then under normal conditions this volume will contain $N_0 V \approx 2.3 \times 10^8$ molecules. The situation that we have noted serves as the basis for using CARS for exact local gas analysis (see Sec. 3).

In spite of the extremely small magnitude of the stated quantities, the efficiency of coherent anti-Stokes scattering can be quite considerable (even at moderate powers of the pump beams). For example, in methane at $p = 1$ atm and $T = 300$ K, we have $(d\sigma/d\Omega) = 1.55 \times 10^{-30}$ cm²/steradian. By using (8) we can estimate: $P_a/P_2 = q_a/q_2 \approx 1.8 \times 10^{-3}$ for $P_1 = 10$ kW. Upon recalculating to the number of photons emitted into the anti-Stokes wave in a time τ equal to the duration of the pulses of pump radiation (we assume that $\tau = 10$ ns), we obtain: $q_a = 5 \times 10^{11}$ for $P_2 = 1$ kW.

It is instructive to compare this quantity with the number of "Stokes" photons q_s emitted under analogous conditions in a spontaneous Raman scheme:

$$\left(\frac{q_s}{q_1}\right)_{\text{SRP}} = \frac{P_s}{P_1} = l_{\text{DOK}} N \frac{d\sigma}{d\Omega} \delta\Omega; \quad (9)$$

Here N is the density of the molecules, and $\delta\Omega$ is the receiving solid angle of the detection apparatus. When $P_1 = 10$ kW and $\delta\Omega = 1$ steradian, we have $(q_s)_{\text{SRP}} \approx 0.6 \times 10^{-11}$, and $(q_a)_{\text{CARS}} \approx 3$. The vast difference between the quantities cited illustrates one of the fundamental advantages of CARS over spontaneous Raman spectroscopy.

The list of other important merits of CARS and of most other allied nonlinear-optical schemes, which confer broad prospects on these spectroscopic methods in practical gas analysis, includes the following.

1. In the anti-Stokes variant of CARS, on which we have mainly focused our attention, the signal has a frequency exceeding that of the pump waves. Consequently it lies in a spectral range free from parasitic stray radiation of Stokes luminescence and thermal radiation. An analogous merit is shown by the scheme that involves the effect of inverse Raman scattering (SRLS). An additional merit of CARS is the high collimation of the coherently scattered signal (its divergence practically coincides with that of the pump beams). This makes possible extremely efficient spatial filtration of the useful signal from the background of incoherent stray light and noise (for example, that arising from light scattering of the pump rays by dust or aerosols in the gas under study, emission from solid particles heated by the laser radiation, etc.).

2. The spectral resolution in CARS is determined only by the widths of the lines of the pump lasers, and it can be as small as 0.001 cm⁻¹ (see below), whereas in spontaneous Raman scattering the resolution is restricted by the apparatus function of the spectral instrument, usually lying in the range of several cm⁻¹. This property of CARS is especially important in studying rarefied gases, since there the typical line widths amount to 0.01 – 1 cm⁻¹.

3. The spatial resolution of CARS is determined by

the dimensions of the region of intersection of the interacting focused beams. In the limit, it is restricted only by the pump wavelength. The time resolution is determined by the duration of the employed laser pulses, and it can attain values of $\tau \approx 0.3$ ps.¹⁰⁻¹²

4. Since the power of the coherently scattered signal determined by (7) depends on the equilibrium difference in the occupancies of the initial and final levels of the Raman transition [see (4) and (5)], CARS enables one to perform accurate local measurements of the vibrational and rotational temperatures of gases, including flames, electrical discharges, as well as plasmas.

The merits and defects of the methods of active and spontaneous Raman spectroscopy are discussed in greater detail in Sec. 7 from the standpoint of analyzing the signal-to-noise ratio.

As we have noted above, the main defect of CARS, which is most distinctly manifested in studying strongly compressed or overheated gases and also in detecting small concentrations of impurity molecules in an atmosphere of buffer gases, is the existence of the nondispersive pedestal in "active" spectra. This is associated with χ^{SNR} , or the nonresonance component of the nonlinear susceptibility (see Fig. 1). If this nonresonance coherent background is not suppressed, then the lower limit for detecting most impurities lies at the level of 1000 ppm or higher.

Therefore the problem of suppressing the nonresonance background and enhancing the relative contribution χ^{SR} of the molecular resonance being studied to the overall nonlinear optical susceptibility of the gas is central in detecting trace impurities and in studying broadened or weak Raman resonances by using active spectroscopy. It has recently been solved successfully (see Sec. 3). We note that this problem does not arise at all in the other coherent methods that deal with the dispersion of the imaginary component of the total cubic susceptibility of the medium (SRGS + SRLS, coherent Raman ellipsometry, etc.; see Sec. 6).

In low-pressure gases in which the fundamental mechanism of broadening of Raman lines becomes the inhomogeneous Doppler broadening, the laser-induced redistribution of the occupancies of the individual states of the vibrational-rotational transition under study can become appreciable in the high-power pulsed fields employed for pumping CARS. That is, the equilibrium occupancy distribution breaks down. In a number of applications of CARS, especially in CARS thermometry, this effect is undesirable, and to diminish it one must reduce the intensity of the pump waves. In turn, this reduces the efficiency of coherent scattering and decreases the sensitivity of CARS. Just as in other situations in which a saturation effect must be suppressed, it can prove effective here to go over to quasi-noise pumping. One can gain a certain effect also if, as before, one employs high-power pulsed radiation as one of the pump waves, while the other is the weak radiation of a continuous or quasicontinuous laser (see also Sec. 7).

2. EXPERIMENTAL TECHNIQUE OF CARS

The invention and rapid development of tunable-frequency lasers enables the start in 1972 of experimental studies by the CARS method. Thus, our study⁶ stressed the vast analytical potentialities of active spectroscopy and proposed this very term. We demonstrated experimentally the considerable increase in the intensity of the scattered component when biharmonic pumping was applied. The first studies on CARS in the gas phase were performed by Taran and his associates.^{16,24} Different variants of the experimental apparatus are contained in the cited studies, and also in Refs. 2, 14, 15, 30, 35, 36, 45, and 47.

As an example, let us examine in greater detail an apparatus designed for studies by the CARS method on gas discharges and flames that was developed in the Naval Research Laboratory of the USA^{14,15} (Fig. 2). A commercial Nd³⁺:YAG laser radiating optical pulses with $\lambda = 1.06 \mu\text{m}$ at a frequency of 15 Hz with 70 MW power with a duration of 10 ns in a single transverse mode is employed as the master laser. The radiation of the master laser is converted to the second harmonic in a KDP crystal with an efficiency of about 30%. Here the width of the radiation line at $\lambda = 532 \text{ nm}$ amounts to 0.1 cm^{-1} . The radiation at the fundamental frequency not converted in the first crystal is "doubled" again in a KDP crystal (see Fig. 2), and serves to pump a dye laser in which a diffraction grating (echelette) with 316 lines/mm is used as the frequency selector to make possible a width of the laser line of 0.25 cm^{-1} . This fixes the spectral resolution of the apparatus. After amplification in a one-pass amplifier pumped by a fraction of the $\lambda = 532 \text{ nm}$ radiation, the radiation of the dye laser (ω_2) has a power up to 500 kW, and is spatially combined in the sample under study with the radiation at $\lambda = 532 \text{ nm}$ (ω_1).

The detected signal at the frequency $\omega_a = 2\omega_1 - \omega_2$ is fed through a system of filters to a photodetector from which the current pulse is applied to the input of an integrator. The signal from the photodetector recording the amplitude of the pulses of the dye laser is applied to the second input of this integrator. The signals at the frequencies ω_a and ω_2 are averaged in the integrator, and one signal is normalized to the other to diminish the effect of fluctuations in the amplitudes of the laser pulses. The spectra are recorded on a strip-chart recorder connected to the output of the integrator.

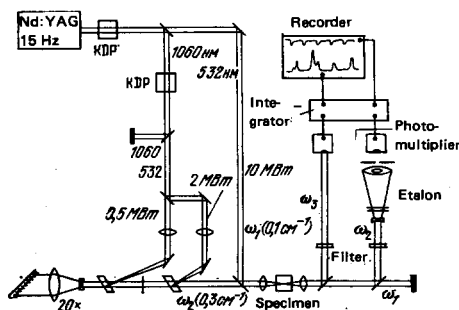


FIG. 2. Apparatus developed in the Naval Research Laboratory of the USA for CARS spectroscopy in gases.

tor, with the chart speed synchronized with the frequency scanning of the dye laser.

An analogous apparatus designed for analyzing flames by the CARS method has been built by Taran and his associates at ONERA (France)¹⁹ (Fig. 3). In contrast to the apparatus in Fig. 2, this apparatus¹⁹ contains a comparison channel. This enables one to diminish the effect of fluctuation of the parameters of the pump waves on the recorded spectrum. Various polarization devices ($\lambda/2$ and $\lambda/4$ plates, Glan-Thomson prisms) are employed in the apparatus in Fig. 3 to suppress the coherent background that restricts the sensitivity of CARS in detecting small concentrations of molecules of interest.

Recently, in connection with progress in the design of minicomputers, the accumulation and processing of spectroscopic information in CARS spectrometers and also the control of the tuning of the generation frequency of the dye lasers have been performed with minicomputers and the corresponding peripheral instruments (see, e.g., Refs. 36, 45, 47). A number of studies (see, e.g., Refs. 42, 43, 66-68) describe apparatus designed for experiments at ultrahigh spectral resolution. The fundamental elements of these apparatus are a continuous-wave ionized-argon or krypton laser and a dye laser excited by the continuous argon laser. The spectral resolution in these instruments usually amounts to 0.001 cm^{-1} . The progress in development of narrow-band dye lasers has made it possible to attain a spectral resolution of 80 MHz with high-power pulsed dye lasers that was limited only by the reciprocal duration of the optical pulse.⁴⁷

3. MEASUREMENT OF THE QUANTITATIVE AND QUALITATIVE COMPOSITION OF STATIONARY GAS MIXTURES USING CARS

The possibility of using CARS and related nonlinear-optical methods as an instrument for quantitative and qualitative gas analysis and for gas thermometry stems directly from the potentialities of the underlying pheno-

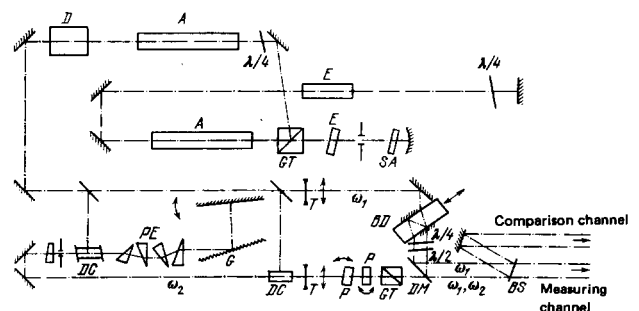


FIG. 3. Diagram of an apparatus developed at ONERA (France) for gas analysis by the CARS method. A—Nd³⁺:YAG laser and amplifier; BD—plane-parallel plate for generating parallel beams; DM, BS—dichroic mirrors; D—frequency doubler for laser radiation based on a KDP crystal; DC—cuvettes containing dye; E—Fabry-Perot etalon; G—diffraction grating; GT—Glan-Thomson prism; P—plates for parallel displacement of beams; PE—beam expander in the dye laser; SA—cuvette containing a saturable absorber; T—telescope, $\lambda/4$, $\lambda/2$ —quarter- and half-wave plates, respectively. The width of the generation line of the dye laser is 0.07 cm^{-1} .

menon of Raman scattering²⁰⁻²³ and needs no special discussion. The new features that the coherent methods introduce into this field of practical gas analysis are related to their advantages noted above in Sec. 1 over spontaneous Raman spectroscopy in the high level of the recorded signal, fast action, high spectral and spatial resolution, and diminished sensitivity to optical interference and parasitic stray light.

These new features were clearly understood even in the first stage of development of studies on CARS, and they were reflected in the reviews of Refs. 4, 15, 24. Here we shall only briefly touch upon the most important of the early studies and take up in somewhat greater detail the later publications.

CARS was first employed in the studies of the group of J. -P. Taran (France) to measure the absolute concentration of impurity molecules in a buffer gas (H₂ in an atmosphere of N₂), to measure the local distribution of molecules of a given sort in stationary jets and flames (in particular, H₂ in the flame of a methane burner), and to measure the spatial temperature distribution in flames.^{16,17,19,24} The great advantages of this method over others were illustrated.

Simultaneously these and other²⁵⁻²⁷ studies elucidated the difficulties that arise in employing CARS to detect extremely small concentrations of an impurity. These are due to the existence of a pedestal in the "active" spectrum arising from the nonresonance susceptibility $\chi^{(3)NR}$ of the molecules of the buffer gas (see Sec. 1). Thus, the limiting detectable concentration of H₂ from the Q₀₁(1) Raman line in an atmosphere of N₂ at $p \approx 1$ atm, $T \approx 300$ K amounted to 40–100 ppm, which is determined by the quantity $(\bar{\chi}^{(3)NR})_{H_2} / (\bar{\chi}^{(3)NR})_{N_2} \approx 1.6 \times 10^4$.²⁸ Other molecules, which have a larger width of the Q-band than H₂ and a smaller Raman cross-section are characterized by a limiting detectable concentration in the range 100–1000 ppm or higher.¹⁷ This substantially restricts the applied potentialities of CARS.

Our papers^{27,29} have proposed a simple polarization method for suppressing this coherent background. It uses the difference in the symmetry properties of the tensors $\chi_{ijkl}^{(3)R}$ and $\chi_{ijkl}^{(3)NR}$ —the resonance and nonresonance components of the cubic susceptibility [see (3)]. As was shown,^{27,30} whenever the pump waves at the frequencies ω_1 and ω_2 are linearly polarized, and their polarization unit vectors e_1 and e_2 lie at a certain angle to one another (usually chosen in the range 45°–70°) (Fig. 4), the polarizations of the signal waves associated with $\chi^{(3)NR}$ and $\chi^{(3)R}$ differ, and the angle between the corresponding polarization unit vectors depends on the angle $\varphi = e_1 e_2$. Figure 4 shows the mutual arrangement of the unit vectors e_1 and e_2 and the polarization vectors P_R and P_{NR} of the signals associated respectively with $\chi^{(3)R}$ and $\chi^{(3)NR}$. If we introduce a polarizing analyzer perpendicular to P_{NR} into the signal being detected, then the nonresonance background will be effectively suppressed, while the useful resonance component of the signal will be only slightly weakened.

The expression for the power of the useful signal in this case has the usual form (7), except that one must

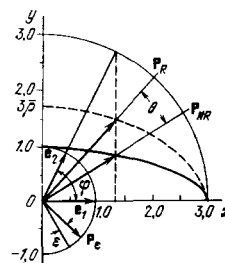


FIG. 4. Relative arrangement of the polarization unit vectors of the pump waves e_1 and e_2 and of the vectors P_R and P_{NR} which correspond to the resonance Raman and nonresonance electronic contributions to the CARS signal. The geometric locus of the ends of these vectors with varying ϕ is: P_{NR} —an ellipse with semi-axes 3 and 1; for P_R —and ellipse with semi-axes 3 and 3ρ ; P_e is the unit vector fixing the plane of the vibrations transmitted by the analyzer; ϵ is measured from the normal to P_{NR} .

take another quantity in place of the term $3\chi^{(3)}$ in it:

$$3(\chi_{1112}^{(3)} - \chi_{1211}^{(3)}) \frac{\sin 2\varphi}{\sqrt{8 \cos^2 \varphi + 1}} = \frac{3}{2} \bar{\chi}^{(3)R} (1 - 3\rho) \frac{\sin 2\varphi}{\sqrt{8 \cos^2 \varphi + 1}}. \quad (10)$$

Here $\bar{\chi}^{(3)R}$ is defined in (5), ρ is the degree of depolarization of the Raman line, and φ is the angle between the polarization unit vectors e_1 and e_2 of the pumps. The power of the anti-Stokes signal is maximized at $\varphi = 60^\circ$ for all ρ .

The gain in sensitivity in detecting trace impurities upon suppressing the "pedestal" by the described method usually amounts to 2–3 orders of magnitude (further increase in the sensitivity is limited by the quality of the focusing optics and of the polarizing devices). Thus, even in our first experiment with gas mixtures²⁹ (an impurity of CO₂ in an atmosphere of N₂), a sensitivity of 100 ppm in the impurity was easily attained, whereas without polarization suppression of the pedestal, the limiting detectable concentration of CO₂ lies at the level of 1000 ppm (Fig. 5).

The described method for discriminating against the

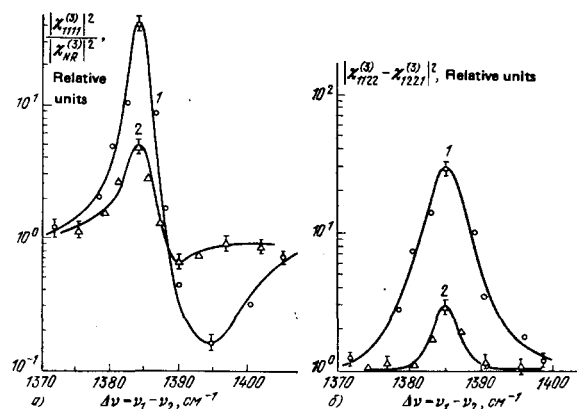


FIG. 5. Dispersion curves of $|\chi^{(3)}(\Delta\nu)|^2$ of a gas mixture of CO₂ and N₂ for various values of n , the relative concentration of CO₂. The difference between the pump frequencies is tuned about the Raman resonance in the CO₂ molecule having the frequency $\Omega/2\pi c = 1388$ cm⁻¹; $\omega_1 - \omega_2 \approx \Omega$. a) CARS without polarization suppression of $\chi^{(3)NR}$ ($1-n = 1 \times 10^{-2}$, $2-n = 1 \times 10^{-3}$); b) with the nonresonance background suppressed ($1-n = 1 \times 10^{-3}$, $2-n = 1 \times 10^{-4}$).

nondispersive coherent background in CARS spectra is now generally adopted.^{19,31-36}

Figure 6 shows the results of the experiments of Rahn and his associates³⁴ (Sandia Laboratory, USA), which distinctly illustrate the increase in "contrast" of active Raman spectra when one employs polarization suppression of the coherent background. Fig. 6a corresponds to the dispersion of the intensity of the anti-Stokes signal in ordinary amplitude CARS (the square root of this intensity is plotted along the ordinate axis, which corresponds to the dispersion of $|\chi^{(3)}(\omega_s; \omega_1, \omega_1, -\omega_2)|$ in the region of the Raman resonance of the CO molecule. Owing to the high pedestal arising from the air molecules, the dispersion of $|\chi_{1111}^{(3)}|$ of the mixture arising from the CO molecules is small. Moreover, it is masked by the instabilities of the amplitude of the anti-Stokes signal arising from the amplitude fluctuations of the pump lasers. Upon eliminating this pedestal by separating the polarization unit vectors of the pump waves by 60° and introducing an analyzer into the anti-Stokes ray that is crossed with the polarization of the nonresonance pedestal, the dispersion of $|\chi^{(3)}|$ in the region of the Q-bands of the CO molecules is manifested in details (Fig. 6b). One can also see the lines of the O-branch of the N_2 molecules at the frequencies 2152, 2143, 2135, 2127, 2118, 2109, and 2100 cm^{-1} . The improvement of the signal-to-noise ratio in Fig. 6b as compared with Fig. 6a is evident, in spite of a certain general decrease in the signal level in the first case. The absence of a coherent pedestal, and correspondingly of interference distortion of the lines in Fig. 6b, considerably simplifies the interpretation of the spectra.

The spectra shown in Figs. 6a, b were obtained from

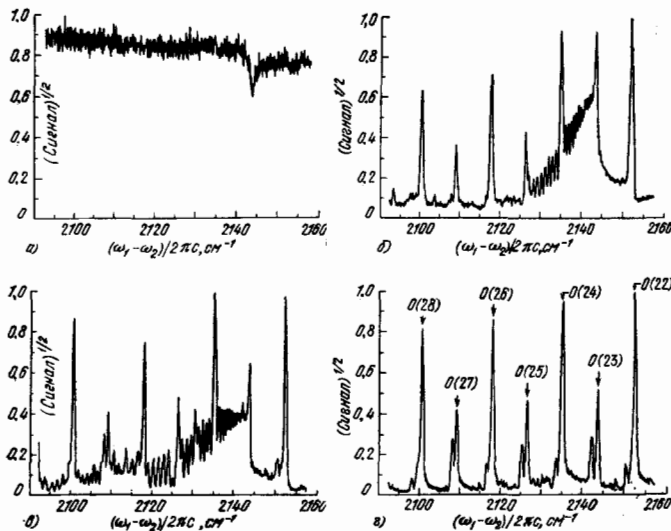


FIG. 6. Increase in the contrast of active spectra of CO in the flame of a methane burner following polarization suppression of the coherent background. a) CARS spectrum at the center of the flame without suppression of the background; b) CARS spectrum at the center of the flame with suppression of the background; c) background-suppressed CARS spectrum 3.2 mm from the center of the flame (in the region of the edge of the flame); d) background-suppressed CARS spectrum 4.2 mm from the center of the flame (outside the flame).

a small volume of gas of diameter 20–30 μm and length ~ 1 –2 mm in the center of the flame of a methane burner. Figs. 6c, d show the CARS spectra obtained in the same geometry and in the same spectral range (with discrimination against the coherent background) from other regions of the flame of this same burner. They offer a clear picture of the decrease in concentration of carbon monoxide from the center of the flame to the periphery. In the active spectrum in Fig. 6d, along with the lines of the O-branch of the vibrational-rotational transitions of the N_2 molecules between the ground ($v=0$) and first excited ($v=1$) vibrational states, we can see also the components of the O-branch of the transitions between the first and second excited vibrational states of N_2 (satellites of the strong lines) (see also Sec. 4).

On the other hand, the existence of the coherent pedestal of the CARS lines arising from the $\chi^{(3)\text{NR}}$ of the buffer gas, as we have already stressed, can be employed as a reference point for absolute measurements of the concentration of the impurity molecules. What we have said is illustrated by Fig. 7, which shows the results of the experiments of Eckbreth and his associates³² (laboratory of the firm "United Technologies," USA). The active spectra of oxygen molecules were obtained at different points near the flame of a plane hydrogen burner (the distance to the point of measurement is measured from the edge of the flame). The shape of the active signal line of the O_2 molecules changes as one moves the point of observation away from the flame. This involves the variation in the conditions of interference in the active spectrum between the resonance contribution $\chi^{(3)\text{R}}$ of the O_2 molecules and the nonresonance susceptibility $\chi^{(3)\text{NR}}$ of the entire gas with varying O_2 concentration [see Eqs. (2) and (3) and Fig. 1]. While the contribution of the O_2 molecules at a distance $y=2$ mm from the flame to the total cubic susceptibility of the mixture was barely noticeable (the O_2 concentration is small), the resonance Raman contribution of oxygen dominates even at a distance $y=3.5$ mm.

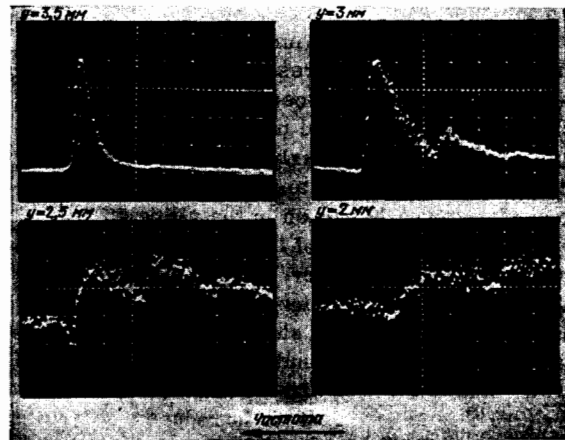


FIG. 7. CARS spectra of O_2 at various distances of the point of observation from the edge of the flame of a hydrogen burner as recorded with an optical multichannel analyzer during a single laser pulse (10^{-8} sec). a) Point of observation 3.5 mm from the flame; b) point of observation 3 mm from the flame; c) point of observation 2.5 mm from the flame; d) point of observation 2 mm from the flame.

In these experiments, just as in the studies cited above,^{19,33,34} a scheme of noncollinear synchronous interaction of the beams in CARS was employed to increase the spatial resolution of the gas analysis (the so-called BOXCARS scheme³⁷). In this scheme the focused pump beams intersect at a certain angle (in order to decrease the length of the interaction region). However, the mean wave vectors of the beams satisfy the vector condition for synchronization: $k_a = k_i + k_j - k_2$ (k_i and k_j are the wave vectors of the intersecting pump beams having the same frequency ω_1).

The large intensity of the CARS signal and the uniquely high spectral resolution, which attains 0.001 cm^{-1} when one uses the radiation of narrow-band stabilized lasers as the pump for CARS, enables one to obtain a fully resolved fine structure of the vibrational-rotational Raman spectra of low-pressure gases. The spectra have been obtained from such gases as H_2 ,^{17,38} N_2 ,^{39,40} O_2 ,^{32,41} CO ,^{31,34,39} CH_4 ,^{42,43} CO_2 ,^{29,44} CD_4 and SiH_4 ,⁴⁵ etc.

As an example, Fig. 8 shows the "active" spectra of high spectral resolution (0.001 cm^{-1}) of the Q-band of the ν_1 vibration of the methane molecule situated in the gas phase at a pressure of 0.5 Torr and a temperature $T = 80 \text{ K}$.⁴² The spectra were obtained by Prokhorov and his associates (P. N. Lebedev Institute of Physics of the Academy of Sciences of the USSR). This same diagram shows the assignment of the spectral lines to the types of transitions in the Q-band of the CH_4 molecules.

We should note that stabilized continuous-wave lasers were employed as the pump lasers in these and most other experiments on high-resolution CARS (see Refs. 42, 43, and 46). These possess relatively low power (up to 10 W in the line of fixed frequency). Consequently the intensity of the CARS signal in this case is relatively low, lying at the level of the signal in spontaneous Raman scattering. The reason why CARS was employed here is the possibility of obtaining ultrahigh spectral resolution.

Recently A. Owyong (Sandia Laboratory, USA) has developed a narrow-band pulsed source of pump radiation for coherent Raman spectroscopy of rarefied gases with an extremely narrow generation line (determined only by the reciprocal of the duration of the generation pulse).^{47,48} The source amounts to a cascade of pulsed amplifiers of the radiation of a continuous-wave single-

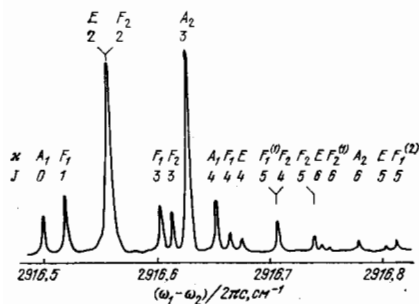


FIG. 8. CARS spectrum of the central part of the Q-branch of the ν_1 vibration of CH_4 (pressure 0.5 Torr, $T = 80 \text{ K}$).

mode stabilized dye laser. At the output of the amplifiers, which are excited with a pulse of the second harmonic of an Nd^{3+} :YAG Q-switched laser, one obtains tunable radiation of power up to 5 MW and with a line width near 80 MHz (0.0025 cm^{-1}) (a system having similar parameters has been described in Ref. 49). As the second pump wave they use the radiation of a continuous-wave single-mode argon laser. Figure 9 shows a sample of a high-resolution spectrum of the Q-band of the ν_1 vibration of SF_6 molecules at $p = 10$ Torr as obtained with the described system (a scheme of SRLS of the high-frequency pump component was employed).

4. PROBING OF EXCITED GAS SYSTEMS, GAS FLOWS, AERODYNAMIC JETS, AND PLASMAS USING CARS

Molecules in excited electronic or vibrational states and the plasma of an electric discharge are an example of other objects in the diagnostics of which CARS has proved to be a highly useful instrument.

The main purpose of CARS here consists of measuring the distribution of occupancies of the excited states, thereby measuring the temperatures of the various subsystems of excited molecular media, and also of determining the temperature, density, and dispersion of a plasma.

The temperature of the rotational and vibrational subsystems of excited molecules is determined from the intensity of the "hot" bands in the active spectra. The principle of observation of these lines is illustrated by Fig. 10 using the example of vibrational spectra. Owing to anharmonicity, the line corresponding to the transition between the vibrational states $v = 0$ and $v = 1$ has a frequency differing from that of the transition $v = 1 \rightarrow v = 2$ and from all the rest of the transitions between excited vibrational states. For the same reasons, the line $v = 1 \rightarrow v = 2$ is not superposed on the line $v = 2 \rightarrow v = 3$, etc. At the same time, the peak intensities of these lines in the active amplitude spectra, which are proportional to the squares of the corresponding peak values of the resonance susceptibilities $|\chi^{\text{GR}}|^2$, in line with the expression (5) for the nonlinear susceptibility, are determined by the difference of occupancies of the initial and final states.

Figure 11 shows a typical active amplitude spectrum of a vibrational-rotational system—nitrogen molecules

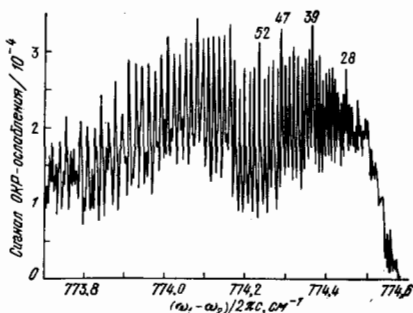


FIG. 9. High-resolution spectrum of the Q-band of the ν_1 vibration of SF_6 at a pressure of 10 Torr as obtained with a SRLS scheme. The powers of the pump laser and the probe radiation were 2 MW and 100 mW, respectively. The rotational quantum numbers J are noted at the top.

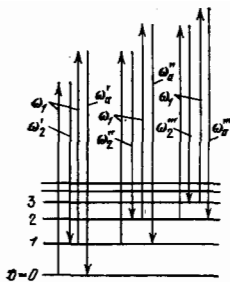


FIG. 10. Diagram explaining the principle of observing transitions between excited vibrational states with CARS.

at a pressure of 4 Torr excited by electron impact in a weak electric discharge. The spectrum was obtained by Smirnov and Fabelinskii.⁵⁰ One can distinctly see the lines corresponding to transitions between the excited vibrational states of the N_2 molecules up to the transition $v=4 \rightarrow v=5$. For each pair of levels let us introduce the effective vibrational temperature $T_{v,v'}$ according to the following formula:

$$\frac{I_v}{I_{v'}} = \frac{N_v^2}{N_{v'}^2} \exp\left(\frac{2h\Omega_{vv'}}{kT_{v,v'}}\right),$$

Here I_v and $I_{v'}$ are the intensities of the lines in CARS corresponding to the transitions $v \rightarrow v+1$ and $v' \rightarrow v'+1$, respectively ($\Omega_{vv'}$ is the frequency of the transition $v \rightarrow v'$, and $N_v \propto (v+1)$, $N_{v'} \propto (v'+1)$ are the occupancies of the levels v and v'). Then the authors⁵⁰ obtained for the described system the following values for the corresponding transitions:

- $v = 0 \rightarrow v = 1$: $T_{0,1} = 2850 \pm 100$ K,
- $v = 1 \rightarrow v = 2$: $T_{1,2} = 3100 \pm 100$ K,
- $v = 2 \rightarrow v = 3$: $T_{2,3} = 3400 \pm 150$ K,
- $v = 3 \rightarrow v = 4$: $T_{3,4} = 3500 \pm 200$ K.

This indicates that the occupancies of the upper levels deviate appreciably from a Boltzmann distribution.

Analogous results showing a considerable deviation of the distribution of occupancies of the highly excited vibrational levels of N_2 in a discharge from the Boltzmann distribution under various experimental conditions had been reported earlier.⁵¹

It was pointed out in the same paper that this situation is not unexpected from the standpoint of a theoretical model that takes into account the anharmonicity of the vibrations.⁵² However, the quantitative disagreement of the experimental and calculated occupancy dis-

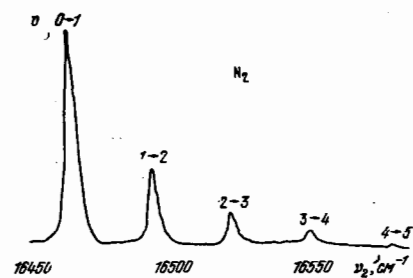


FIG. 11. Vibrational CARS spectrum of N_2 in an electric discharge. Sequence of lines corresponding to the transitions $v=0 \rightarrow v=1$; $v=1 \rightarrow v=2$, etc. Resolution 2 cm^{-1} .

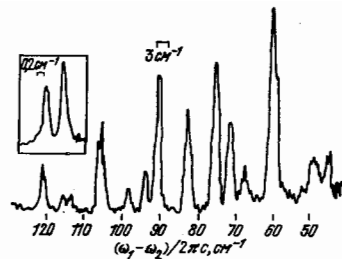


FIG. 12. Pure rotational spectrum of air. The inset shows a region of the spectrum in the region of 60 cm^{-1} as obtained with higher resolution. One can see the close lines of $^{14}N_2 J=6 \rightarrow J=8$ and $^{16}O_2 J=9 \rightarrow J=11$.

tributions apparently indicates a dependence of the excitation cross-section of the molecules for electron bombardment on the vibrational state of the molecule.

CARS is also applicable for measuring the rotational temperature of excited molecules. This can be done in two ways.

First, one can measure the intensity distribution in the pure rotational Raman spectrum of the molecules or in the rotational O-, P-, and R-, S-branches of any vibrational-rotational transition. For example, the active spectrum of rotational Raman scattering of air molecules shown in Fig. 12 can serve for these purposes.

Second, one can measure the intensity distribution in the resolved structure in the Q-branch of the Raman spectrum to determine the rotational temperature of the excited molecules. For example, Fig. 13 shows the experimental spectrogram of the intensity distribution in the Q-branch of the vibrational transition $v=4 \rightarrow v=5$ of N_2 molecules in a discharge under the same conditions as in the spectra of Fig. 11 (except that the line width of the tunable laser was decreased from 2 cm^{-1} for taking the spectra of Fig. 11 to 0.1 cm^{-1} for taking the spectra of Fig. 13 so as to resolve the individual J -components of the Q-band in the latter case). The intensity distribution of the rotational components in this spectrum corresponds to a Boltzmann distribution characterized by a rotational temperature $T = 395 \pm 15$ K. The intensity distribution in all the other Q-bands of the "hot" vibrational spectrum of N_2 in the discharge was described by the same temperature. Thus a considerable gap was found here between the vibrational and rotational temperatures of the N_2 molecules ex-

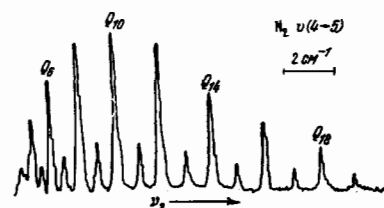


FIG. 13. J -structure of the Q-branch of the vibrational transition $v=4 \rightarrow v=5$ in an electric discharge in N_2 . The intensity distribution of the individual rotational components corresponds to a Boltzmann distribution with a temperature $T_{\text{rot}} = 395 \pm 15$ K.

cited by electron impact. We note in passing that the second of the described methods for determining the rotational temperature is easier to employ in quick measurements by the CARS method with broad-band excitation (see Sec. 5 below), than the first method, because the Q-bands occupy considerably narrower spectral intervals than the rotational O-, S-, and P-, R-wings of the vibrational transitions. Hence the realization of the second method requires tunable lasers with a moderate width of the generation line (in the range $5-10 \text{ cm}^{-1}$).

One of the most promising fields of application of CARS in applied problems is remote nonperturbing local rapid analysis of nonstationary gas jets, reactive flows, and also processes occurring in internal-combustion engines. The high information content of the traditional optical methods, and especially of spontaneous Raman scattering, in solving these problems is well known (see below in Sec. 6, and also Refs. 20-23). However, the weakness of the spontaneous Raman signal and the impossibility of effective spatial filtration of the useful signal greatly complicates or completely renders impossible the application of spontaneous Raman scattering for diagnostics of dust-bearing aerodynamic flows, combustion processes in which the flame is contaminated with solid particles of fuel or soot, etc. Yet it is precisely under these conditions that CARS proves especially effective. This feature of CARS and of other coherent methods of optical gas analysis has recently attracted much attention from specialists in the field of aerodynamics and from engineers concerned with developing and perfecting reactive and rocket motors.

Measurements of the density distribution of molecules of particular types, vibrational and rotational temperatures of various components of gas mixtures, and their absolute and partial pressures have been performed with the various modifications of CARS in the exhaust gases of actual operating reactive and rocket engines and in the air flows of aerodynamic tubes.^{19,32,33,53,55}

Profiles of the vibrational-temperature and pressure distributions were first obtained⁵⁵ by the CARS method in a supersonic gas flow of nitrogen (Fig. 14; diagram of the configurations of the supersonic jet and the laser

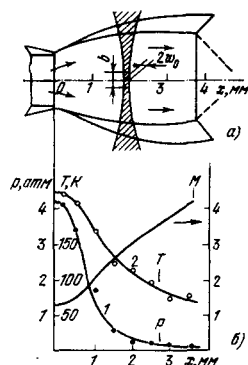


FIG. 14. Study of the parameters of a supersonic jet by the CARS method.

beams (a) and the distribution of local values of the temperature and pressure along the axis of the jet (b); 1-experimental pressure values, 2-experimental temperature values, solid lines-calculated values. M is the calculated value of the Mach number). The spatial resolution was determined by the region in which 95% of the power of the CARS signal was generated. According to the estimates of the authors, it was characterized by a volume of $12 \times 12 \times 500 \mu\text{m}$. The CARS spectra were measured in the region of the Q-branch of the $\nu=0 \rightarrow \nu=1$ transition of nitrogen and were then compared in a computer with the previously determined experimental dependence of the contour of the Q-branch on the pressure and the temperature. An analogous method has been used³² to determine the spatial temperature distribution in the nozzle of a propane burner in the presence of a considerable amount of soot and carbon black in the combustion products. Figure 15 shows the results of this experiment as processed on a computer.

Currently studies along this line are being intensively conducted in a number of large research and industrial laboratories abroad, including the laboratories of the large industrial and defense firms—United Technologies (USA)^{32,53,56,57} the Ford Motor Company (USA),³³ in the research laboratory of the Wright-Patterson Air Force base of the USA,^{58,60} ONERA in France,^{18,19,39} the Sandia Laboratories at Livermore and Los Alamos (USA),^{31,34,47,48} and at the Naval Research Laboratory of the USA,^{15,51,59} etc.

Another important line of employment of the methods of active laser spectroscopy for applied purposes can be the local diagnostics of the parameters of a plasma. A theory of this method has been developed.⁶⁶ It was shown that the application of CARS enables one to develop a universal, sensitive method of laser diagnostics of local parameters of a plasma, such as the density, electronic and ionic temperatures, direction and magnitude of the magnetic field, etc. Here the data on the magnitudes of these parameters are drawn from analyzing the light coherently scattered in the plasma, whose intensity exceeds by a factor of 10^5-10^8 the intensity of the ordinary (Thomson) noncoherent scattering.

5. METHODS OF RAPID ANALYSIS USING CARS

Many of the applications of CARS discussed above require a great speed of action characterized by very short exposures (down to the duration of a single laser pulse: $10^{-8}-10^{-12}$ sec). Methods have already been

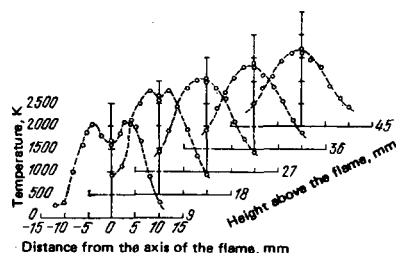


FIG. 15. Spatial temperature distribution in the flame of a propane burner.

developed in CARS relatively long ago that enable one to realize such a great speed of action in practice. To do this, one must go from recording the "active" spectra point-by-point, as was assumed in employing narrow-band tunable lasers as the pump waves ω_1 and ω_2 , to recording the "active" spectra within one laser pulse by employing the modification of CARS involving broadband excitation proposed in our papers.^{2,25} In this case one of the pump waves (assumed to have frequency ω_2) must consist of the radiation of a laser having a very broad uniform spectrum which, when combined with the monochromatic pump wave ω_1 , "covers" the entire spectral region occupied by the Raman lines of the given medium that are of interest to the experimenter.

Here the spectrum of the coherent anti-Stokes signal also proves to be broad. Its form is determined by the product of the contours of the spectra of the broad-band pump and the spectral dependence of the square of the modulus of the cubic susceptibility $|\chi^{(3)}|^2$ of the medium. In order to extract the data on the dispersion of $|\chi^{(3)}|^2$, one should normalize the active anti-Stokes spectrum to the corresponding spectrum of the broad-band pump. Since the broad-band anti-Stokes spectrum is characterized, just like every active spectrum, by a high spectral brilliance, it can be photographed without difficulty or recorded in the memory of an optical multichannel analyzer in one laser flash, i.e., in a time equal to its duration (from 10^{-8} to 10^{-12} sec).

Thus, Taran and his associates²⁸ applied a broad-band dye laser and a narrow-line ruby laser for studying the structure of the Q-band of H_2 . The spectrum was recorded with a multichannel analyzer during one laser pulse ($\tau \approx 10^{-8}$ sec). This method can be successfully applied in studies where one must know the dynamics of the variation in real time of the vibrational spectra of molecules, e.g., in studying fast chemical reactions or temperature variations in turbulent flames. A study was also performed in Ref. 58 on the pressure-dependence of the width of the Raman line of H_2 . Here the spectrum was taken within a time of the order of a single laser pulse. Good agreement is observed with direct measurements in H_2 , D_2 , and CH_4 performed by the CARS method with a spectral resolution of 10^{-3} cm^{-1} .

Figure 16 shows the results of an experiment by Eckbreth *et al.*³² on rapid thermometry by CARS with broad-band excitation of a gas flow emerging from a nozzle where a liquid fuel is being burned. The spec-

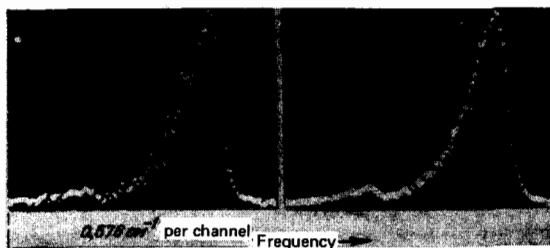


FIG. 16. Comparison of the averaged spectrum of the Q-band of N_2 (right) and of the spectrum taken in one laser pulse of 10^{-8} sec (left).

trum at the left (Q-band of nitrogen) was obtained in one laser flash ($\tau = 10$ ns), and the spectrum at the right by averaging over 130 flashes. Both spectra were taken from the screen of an optical multichannel analyzer (OMA) with a spectral resolution of 0.576 cm^{-1} per channel. In the former case the shape measurements of the spectrum gave a temperature of 1520 K, and 1450 K in the latter case. These numbers characterize the contemporary level of accuracy of such measurements.

6. NEW SCHEMES OF GAS ANALYSIS USING TUNABLE LASERS

Although, undoubtedly, the scheme of coherent amplitude active Raman spectroscopy with generation of anti-Stokes components is currently the best developed and popular among the nonlinear-optical methods of quantitative and qualitative analysis of gaseous media, it is not the only method, nor the most preferable one, in solving all problems without exception in practical spectral analysis. In a number of cases other nonlinear-optical schemes can prove more suitable, and we shall proceed to characterize them briefly in this section.

First of all, in CARS itself various polarization modifications often prove most effective, primarily coherent Raman ellipsometry.³⁰ In this case one is interested in the variation in the polarization state of the coherently scattered Stokes or anti-Stokes signal on passing through a Raman resonance. Owing to the independence of the polarization state of the recorded signal from the intensities of the pump waves, this scheme proves free from a strong source of errors, such as the intensity fluctuations of the exciting waves are in ordinary amplitude CARS. A practical variant of coherent ellipsometry is a scheme in which the variation of the polarization state of the coherent signal is recorded by measuring the ratio of intensities of the components of the signal having mutually orthogonal polarizations.^{35,36} This scheme can be easily automated. Another important class of nonlinear-optical methods of spectral analysis is composed of the methods of laser modulation spectroscopy in which the linear optical parameters of the medium being studied (e.g., the dielectric permittivity) are modulated via the optical nonlinearity.³¹ In this case one extracts spectroscopic information about the material by detecting variations of the amplitude (polarization, phase) of one of the pump waves (say, at the frequency ω_1) induced by the existence in the medium of the other pump component (ω_2). Phenomenologically, such an optically induced variation in the properties of the medium for the wave at ω_1 in the presence of the wave at ω_2 can be described as a modulation of the dielectric permittivity of the medium at the frequency ω_1 owing to the field of the pump wave at the frequency ω_2 : $\hat{\epsilon}(\omega_1) = \hat{\epsilon}_0(\omega_1) + \hat{\epsilon}_2 |E^{(2)}|^2$, where $\hat{\epsilon}_0(\omega_1)$ is the linear component of the dielectric permittivity, $E^{(2)}$ is the amplitude of the field having the frequency ω_2 , and $\hat{\epsilon}_2 = \hat{\epsilon}_2(\omega_1, \omega_2)$ is a coefficient associated with $\chi^{(3)}$ and possessing an appreciable frequency dispersion upon tuning, e.g., the frequency difference $\omega_1 - \omega_2$ over a region of Raman resonances.

The tensor $\hat{\epsilon}_2(\omega_1, \omega_2)$ has the following form: $[\epsilon_2(\omega_1, \omega_2)]_{ijk} = 24\pi\chi_{ijk}^{(3)}(\omega_1; \omega_2, \omega_1, -\omega_2)e_j^{(2)}e_k^{(2)*}$, where the $e_j^{(2)}(j, l = x, y, z)$ are the Cartesian components of the polarization unit vector of the pump wave ω_2 . In the case of Raman resonances with $(\omega_1 - \omega_2) \approx \Omega$ in which we are interested, the resonance behavior of the susceptibility $\chi_{ijk}^{(3)}(\omega_1; \omega_2, \omega_1, -\omega_2)$ is the same in nature as the dispersion for $\omega_1 - \omega_2 \approx \Omega$ of the "anti-Stokes" susceptibility $\chi_{ijk}^{(3)}(\omega; \omega, \omega_1, -\omega_2)$ that we have been treating thus far. That is, it involves the excitation of coherent molecular vibrations in the field of the biharmonic pump. However, now this situation is manifested in the variation of the parameters of the probe wave (ω_2), rather than in the generation of Stokes or anti-Stokes components of scattered light, as in CARS. Since, in a four-photon process of this type, i.e., in a process of the type $\omega_1 = \omega_1 + \omega_2 - \omega_2$ the conditions for spatial synchronization are satisfied identically: $k_1 \equiv k_1 + k_2 - k_2$, and hence, the wave detuning of the process is zero: $\Delta k = 0$, the directions of propagation of the waves ω_1 and ω_2 can be arbitrary, e.g., opposed. This constitutes one of the fundamental advantages of all the schemes of modulation spectroscopy over the different variants of CARS.

In the amplitude variant of laser modulation spectroscopy, one measures the amplification (attenuation) of the low-frequency ω_2 (or high-frequency ω_1) probe wave in the field of the high-frequency ω_1 (low-frequency ω_2) pump wave as the frequency difference $\omega_1 - \omega_2 \approx \Omega$ is tuned. This method has been known for a long time in nonlinear spectroscopy, and is called amplification (attenuation) caused by stimulated (or inverse) Raman scattering, or stimulated Raman gain (or loss) spectroscopy.⁶²⁻⁶⁵ The type of spectrum and the line shape of the SRGS signal are determined by the form of the dispersion curve of the imaginary component of the tensor $(\hat{\epsilon}_2)_{ijk}$, i.e., ultimately by the dispersion of the imaginary component of the susceptibility $\chi_{ijk}^{(3)}(\omega_1; \omega_2, \omega_1, -\omega_2)$, which simultaneously determines both the general type and the form of the spontaneous Raman spectrum. The form of the SRS line practically coincides (apart from sign) with that in the SRGS scheme.

The relative simplicity of the optical scheme, the absence of a pedestal in the SRGS spectra, the possibility of counterpropagation of the interacting beams, and the linearity of the measured signal with respect to the number of particles constitute the major merits of this method. It is being employed ever more widely for spectroscopic measurements, and in particular, for gas analysis.⁶⁶⁻⁶⁸ The possibility exists of employing this scheme for remote probing of the atmosphere, and in particular, for amplifying the spontaneously back-scattered radiation.

The defects of the SRGS scheme include its relatively high sensitivity to amplitude fluctuations of the laser radiation (for more details, see Sec. 7).

One can get very good results in detecting very small quantities of molecules by their Raman spectra by SRGS (this involves the possibility of detecting monomolecular layers on the surface of solids) if one pumps with

the radiation of continuous-wave tunable lasers with synchronized longitudinal modes and with high-frequency amplitude or phase modulation.^{12,70,81} Moreover, under these conditions, also the sensitivity of the other nonlinear-optical methods will be just as high as in the SRGS scheme.

The polarization variant of modulation Raman spectroscopy has recently become ever more widespread. Here one measures the variation of polarization state of the probe beam (say, at frequency ω_1) in the presence of the pump wave (ω_2) as the frequency difference $\omega_1 - \omega_2$ is scanned through the region of Raman resonances: $\omega_1 - \omega_2 \approx \Omega$. This variant has been called spectroscopy based on the optical Kerr effect induced by a Raman resonance (Raman-induced Kerr-effect spectroscopy—RIKES^{71,72,92}). One obtains especially good results that resemble CARS in signal-to-noise ratio when one uses this scheme in combination with optical heterodyning of the detected signal (the so-called OHD-RIKES scheme^{73,92}). The latter enables one to increase the signal-to-noise ratio considerably (as compared with the SRGS scheme), even when one uses lasers poorly stabilized in amplitude. Just like all other varieties of modulation spectroscopy, this variant of nonlinear spectroscopy does not require special means for satisfying the synchronization conditions. In the variant with optical heterodyning, one can separately measure the dispersion curves of the real and imaginary components of the cubic susceptibility tensor $\chi_{ijk}^{(3)}(\omega_1; \omega_2, \omega_1, -\omega_2)$. However, if one does not employ optical heterodyning, one measures the dispersion of the square of the modulus of a combination of several components of this tensor.

In a number of cases optoacoustic measurement of the Raman spectra of gases may prove convenient.^{74,75,93,94} Here one detects the acoustic perturbation caused by the dissipation of energy of the pump light waves owing to resonance pumping of the intramolecular vibrations in the biharmonic light field. Here again one must use the radiation of tunable modulated lasers to excite the intramolecular vibrations. However, this effect is measured by acoustic, rather than optical methods.

In spite of the relative poor noise characteristics of the acoustic receivers, as compared with photodetectors, and especially with photomultipliers, and the relatively low speed of action, the use of an optoacoustic scheme for measuring Raman spectra is attractive in its simplicity, lack of requirements of phase synchronization, and possibility of recording low-frequency optical modes.

A scheme of nonlinear spectroscopy based on measuring the change in the refractive index of the medium owing to local heat release (the so-called light-induced thermal lens method⁹⁰) possesses analogous merits. It potentially has an even greater sensitivity than the optoacoustic scheme, since it is less subject to restriction arising from accompanying nonlinear effects (such as electrostriction in the optoacoustic scheme of detection⁹⁰).

7. COMPARISON OF THE POTENTIALITIES OF CARS AND OF SPONTANEOUS RAMAN SCATTERING IN GAS ANALYSIS

Thus far, in speaking of using optical methods for gas analysis, we have paid major attention to nonlinear-optical laser methods, and first of all, to the different variants of coherent active Raman scattering of light. However, for a correct estimate of the promise offered by some particular method of optical spectroscopy for purposes of gas analysis, it is expedient to compare them with respect to an entire set of parameters. In Secs. 1-5 of this review we have stressed the merits of CARS, while insufficiently exposing the defects of this scheme. In this section we shall attempt to give a more balanced estimate of the two methods, and shall start by briefly reviewing the recent successes of spontaneous Raman spectroscopy in the analysis of gas mixtures.

Currently, spontaneous Raman scattering of light is widely employed in gas analysis to measure the concentration and temperature of individual components in gas flows and flames and for remote probing for atmospheric pollutants (see, e.g., Refs. 4, 76, and 77). Thus the invention of a Raman lidar has been reported⁷⁷; the gases SO_2 , CO_2 , NO_2 , and H_2O have been measured with it at a distance of 200 m in the effluent plume of one of the power plants of Moscow. Concentrations of the individual gases were measured at a level of 50-500 ppm, and the time of analysis amounted to 3-5 minutes. The possibility of remote analysis of gas mixtures confers certain advantages on spontaneous Raman scattering as compared with CARS, though the latter method has 10-100 times greater sensitivity under laboratory conditions, while allowing one to perform exhaustive measurements in a time of 10^{-1} - 10^{-3} sec.

Recently spontaneous Raman scattering with excitation of the spectra with high-power (up to 16 W) continuous-wave ion lasers has been successfully applied to probing gas flows (see Refs. 78-82). Thus, fast Fourier analysis of the intensity of the Raman signal has been employed⁷⁸ to measure the fluctuations in the concentrations of N_2 and CH_4 in a non-steady-state gas flow. The mean concentration of the stated gases was measured, as well as the amplitude and frequency dependence of the concentration fluctuations about the mean as a function of the velocity of the flow and the position of the focal volume of the exciting laser with respect to the gas nozzle. An appreciable difference in the Fourier spectra of the signals from N_2 and CH_4 was observed, as well as an increase in the amplitudes of the concentration fluctuations of the two gases as the point of observation was moved away from the nozzle. The recording of the Fourier spectrum of the fluctuations of the Raman signal was performed in the range of 100 Hz, and the total time for each recording was 65 sec. The defects of the method might include its insufficient sensitivity, which does not allow one to study the components of a gas mixture having a partial pressure below several Torr. Nevertheless the authors⁷⁸ consider the method promising for studying flames. In particular, they note the possibility of

studying the correlation of the fluctuations of the individual components of a gas mixture. We note that in amplitude CARS, whose signal intensity is proportional to the square of the density of molecules, the density fluctuations can give rise to "excess" fluctuations of the signal, similarly to those well known in other branches of nonlinear optics.^{83,84} This can be used effectively in studying the statistical properties of a medium.

A number of authors (see, e.g., Refs. 79-82 and 85) have studied the spatial concentration distribution of individual components in gas flows by the spontaneous Raman method, and also have measured the vibrational temperature of gases in laminar flames. In view of the specific properties of spontaneous Raman scattering, this method enables one to determine the distribution of gases at concentrations no lower than 1000 ppm, and only in stationary two-dimensional gas flows without traces of dust or soot, i.e., under considerably less "real" conditions than are accessible to CARS.

The vibrational temperature of various gases in flames is measured^{79,81,85} by fitting the spectrum calculated on a computer to the experimentally obtained spectrum of the Q-band of the appropriate gas. We should note that the extraction of the needed data from spontaneous Raman spectra involves a less complicated computation procedure than for CARS spectra. The reason for this is the substantial role of interference effects in shaping the contour of the spectral line of the coherently scattered light and the absence of these effects in spontaneous Raman spectra. For example, the ratio of the intensities of the Stokes and anti-Stokes lines in spontaneous Raman scattering directly yields a measure of the occupancies of the excited vibrational states, and thereby a measure of the vibrational temperature. This same ratio in CARS is sensitive also to interference with close-lying transitions, and also to interference of the resonance and non-resonance contributions to $\chi^{(3)}$. In spite of this complication, effective methods have been developed now for calculating active spectra that enable one to perform a complete quantitative "fit" of all details of complicated CARS spectra of real gases at elevated temperatures.⁵⁷ We note in passing that, owing to their complexity and great sensitivity to changes in the various parameters of real molecules, CARS spectra yield richer spectroscopic information about the gas under study than spontaneous Raman spectra do.

In spontaneous Raman spectroscopy, just as in CARS, one can get complete Raman spectra of the materials being studied with a relatively great speed of action in the range of durations 10^{-3} - 10^{-5} sec. Usually high-power pulsed solid-state lasers and sensitive multi-channel recorders combined with high-aperture collecting optics and high-quality spectrographs are employed for obtaining rapid spontaneous Raman spectra. Good results are obtained by employing in the recording system strobed panoramic brightness amplifiers with an input sensitivity of several photoelectrons per resolvable element of the spectrum. By using this technique, the authors of Ref. 86 were recently able to obtain the anti-Stokes Raman spectra of SF_6 molecules in highly

excited vibrational states that were attained for a short time under the action of a high-power resonance infrared pump.

However, the employment of the method of spontaneous Raman scattering in problems of Raman analysis of short-lived excited molecular states seems less preferable than the application here of CARS, primarily owing to problems caused by the small signal-to-noise ratio in spontaneous rapid spectrometers.

As we have noted, the fundamental characteristics of the coherently scattered CARS signal and the spontaneous Raman signal differ [see Eqs. (8) and (9) in Sec. 1 for the intensity]. Therefore one can prefer in different situations the one or the other method, depending on the specific experimental conditions. In a number of cases it is better justified to employ some variant of coherent modulation spectroscopy.

We shall compare the characteristics of CARS, of a scheme based on SRGS (or SRLS), and spontaneous Raman spectroscopy by analyzing the signal-to-noise ratio S/N in each of these schemes.

One can show (see, e.g., Ref. 3, Chap. VI) that the quantum limit of the ratio S/N , which is governed by the shot noise of the photocurrent and the quantum nature of light, is practically identical in CARS and in SRGS (apart from a factor of 1/2) when other conditions remain the same. However, these schemes are not equivalent with respect to sources of "classical" noise, and primarily with respect to intensity fluctuations of the pump waves and the probe ray.

The expressions for S/N have the following form for the corresponding schemes:

$$\text{CARS: } (S/N)_{\text{CARS}} = \frac{G_0}{\sqrt{(4\varepsilon_1 + \varepsilon_2) G_0^2 + 4(\hbar\omega_0 \Delta\nu / \eta P_2)}} \quad (11)$$

(with the coherent background suppressed),

$$\text{SRGS: } (S/N)_{\text{SRGS}} = \frac{G_0}{\sqrt{\varepsilon_1 G_0^2 + \varepsilon_2 + (\hbar\omega_2 \Delta\nu / \eta P_2)}}; \quad (12)$$

Here

$$G_0 = \frac{384\pi^3}{c\lambda} I_1 \bar{X}^{(3)RL}$$

is the value of the integral SRGS amplification at the center of the line, I_1 is the intensity of the pump wave at the frequency ω_1 ; ε_1 and ε_2 are the relative dispersions of the intensity fluctuations of the waves ω_1 and ω_2 in the band $\Delta\nu = 1/T$, which is defined by the time constant T of the measuring channel, and L is the length of the interaction region. Equations (11) and (12) have not taken into account the noise associated with the dark currents of the photoreceivers and the thermal noise of the load resistances. The last terms in the denominators of (11) and (12) describe the "quantum" noise in the band $\Delta\nu$. In these terms η is the quantum efficiency of the photocathode of the receiver used for detecting the signal, $\hbar\omega_1$ and $\hbar\omega_2$ are the corresponding quantum energies, and P_2 is the total power of the wave at frequency ω_2 .

We see from the expressions (11) and (12) that the quantum limits of sensitivity are realized when $G_0^2(4\varepsilon_1$

$+ \varepsilon_2) \ll 4\hbar\omega_0 \Delta\nu / \eta P_2$ in CARS, or when $G_0^2 \varepsilon_1 + \varepsilon_2 \ll \hbar\omega_2 \Delta\nu / \eta P_2$ in SRGS. If $G_0 \ll 1$ (as in most experiments that do not have too powerful pump pulses), we see that the quantum limit in S/N is more easily attainable in CARS than SRGS.

To simplify the analysis we shall assume henceforth that the quantum limit in S/N has been reached in both schemes of coherent spectroscopy. In line with (5), (11), and (12), we have

$$(S/N)_{\text{CARS}} = \frac{1}{2} (S/N)_{\text{SRGS}} \approx \frac{2\lambda^3}{\pi c} \frac{LN}{\hbar\Gamma} \frac{d\sigma}{d\Omega} I_1 \sqrt{\frac{\eta P_2}{\hbar\omega_2 \Delta\nu}}. \quad (13)$$

We should compare this value with the quantum limit of S/N in spontaneous Raman scattering:

$$(S/N)_{\text{spont}} \approx \sqrt{\frac{LN\eta}{\hbar\omega_2 \Delta\nu} \frac{d\sigma}{d\Omega} P_1 \delta\Omega}, \quad (14)$$

Here $\delta\Omega$ is the receiving solid angle, N is the density of molecules, P_1 is the power of the pump at ω_1 , and the rest of the symbols are standard.

Recently Rahn *et al.*⁸⁷ have compared the various methods from the standpoint of sensitivity for detecting molecules of an impurity in a buffer gas at a given value of S/N (with the example of CO molecules in air). Depending on the temperature and pressure of the mixture, one can characterize this sensitivity by the quantity

$$d = N/N_{\text{imp}}$$

Here N is the total density of molecules of the mixture, and N_{imp} is the density of impurity molecules.

It is of greatest practical interest to compare the values of the detecting power d of the various methods under conditions in which all the parameters of the corresponding spectroscopic schemes are optimized.

In the coherent schemes, the optimal choice will be that of the maximum possible intensities of the pump waves at which breakdown of the gas has not yet set in and the thresholds have not been exceeded for stimulated scattering, autofocusing, and other undesirable phenomena. The most serious problem is presented by optical breakdown of the gas, whose threshold is depressed by increasing density of the gas, approximately by the law $\rho^{-0.57, 88}$. In the calculations of Ref. 87 it was assumed that the intensity of one of the pump waves in CARS and in SRGS is taken to be half the threshold for optical breakdown. The intensity of the second pump wave in CARS has an upper bound in the requirement that the interaction of the pump waves should not destroy the equilibrium distribution of the molecules over the levels to a certain accuracy Z . The expression for the relative fraction $\Delta N/N$ of molecules excited in the biharmonic pump field of CARS has the form

$$Z = \frac{\Delta N}{N} = \frac{\lambda^4}{2\hbar^2 \Gamma} \frac{d\sigma}{d\Omega} \frac{I_1 I_2}{c^2 \pi^2} \tau. \quad (15)$$

Here τ is the duration of the pump pulses, 2Γ is the homogeneous width of the transition being studied, and the rest of the symbols are standard. Upon fixing I_1 and Z , one can determine from (15) the optimal value of I_2 .

The perturbation of the equilibrium occupancy of

the vibrational (or rotational) transition in the biharmonic pump field of CARS described by (15) strongly limits the sensitivity of CARS at low pressures of the gas mixture, for which the homogeneous "collisional" width 2Γ of the transition is small. We have already noted above (see Sec. 1) that here, just as in other variants of nonlinear spectroscopy influenced by the saturation effect,⁸⁹ one can considerably restrict the "movement" of the occupancies of the studied transition that we have noted. Thus the sensitivity of CARS is substantially elevated if one employs as the pump ω_2 a sufficiently broadband radiation with a relatively small spectral intensity density: $I_1/\Delta\omega_2 \leq (I_2/\Delta\omega_2)_{\text{sat}}$.⁸⁹ However, in the calculations of Ref. 87, both pump lines of CARS were assumed considerably narrower than the collisional width of the transition under study. This is not an optimal choice.

In the case of SRGS, the calculations assumed a quasicontinuous scheme in which the second pump wave (or the probe wave) consisted of the focused radiation of a 10-W continuous-wave laser (in principle, one can use the same method in CARS). Here no problems arise involving saturation of the transition under study. The dimensions of the focal region of the lens that focused the pump radiation inside the studied gas was considered invariant and limited only by diffraction. The relationship of the width of the Raman line to the pressure (density) and temperature was taken in the form of (6). The temperature-dependence of the equilibrium occupancy difference of the vibrational-rotational transitions and the "switching-on" of an inhomogeneous Doppler broadening at low pressures were also taken into account.

Figure 17 shows the results of these calculations. The values of the parameters employed in the calculation are indicated in the caption.

The variations that are presented reveal first of all the complementary character of the spontaneous and co-

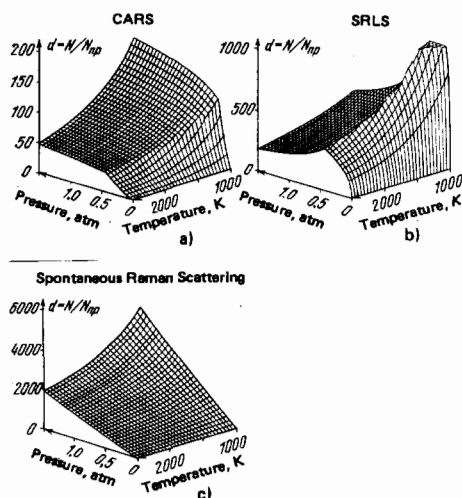


FIG. 17. Calculation of the sensitivity limit for detecting CO in fuel-combustion products for different methods of detection. $\Omega/2\pi c = 2413 \text{ cm}^{-1}$, $\tau_{\text{pulse}} = 6 \text{ ns}$; $\Gamma/2\pi c = 0.1 \text{ cm}^{-1}$, $S/N = 10$. a) CARS with suppression of the coherent background ($\delta\sigma = 1.8 \times 10^{-4}$ steradian); b) SRLS ($\delta\sigma = 1.8 \times 10^{-4}$ steradian); c) spontaneous Raman scattering ($\delta\sigma = 0.2$ steradian).

herent methods in Raman spectroscopy: under conditions in which the sensitivity of any one of the methods declines, the sensitivities of the others show a "plateau" or a rise.

The declining sensitivity of CARS and SRGS with increasing gas temperature (at fixed p) mainly involves the broadening of the Raman resonance line and the parallel decline in $\bar{\chi}^{\text{CR}}$, as well as the decreased occupancy differences of the vibrational transition. The sharp decline in the sensitivity of CARS in the low-pressure region is due to the "switching-on" of the inhomogeneous Doppler mechanism of line broadening. This leads to a need to decrease the peak values of the intensities of the pump waves, so as to avoid saturating the transition under study. This situation is practically not manifested in the SRGS scheme, since here the radiation of a low-power continuous-wave laser is taken as the probe beam.

In the calculations that were performed, the powers of the beams were maximal in the region of low pressures and high temperatures. However, even here they did not exceed 5 MW for the pump ray ω_1 and 1 MW for the tunable CARS pump wave ω_2 . That is, they do not exceed the limiting values that one can obtain with standard Q-modulated lasers.

The dependence of the sensitivity of spontaneous Raman scattering on T and p coincides with the dependence of the density of the gas on these same quantities. The calculations assumed that the spontaneous Raman spectra are excited with a continuous-wave laser of 10 W power, the scattered radiation is collected within a solid angle $\delta\sigma = 0.2$ steradian, while the monochromator completely transmits the spectral interval occupied by the entire Q-band of the CO molecules (i. e., resolution of the individual J -components of the Q-band is not assumed here). We must note that the sensitivity of spontaneous Raman scattering depends strongly on the required value of the signal-to-noise ratio, on the receiving solid angle, and especially on the spectral resolution. For example, if instead of the values employed in the calculations we take $(S/N)_{\text{spont}} = 40$, $\sigma = 0.1$ steradian, and require a spectral resolution of the order of 1 cm^{-1} , then the sensitivity of spontaneous Raman scattering will fall to a level about 200 times lower than the sensitivity of CARS and SRGS under analogous conditions.

Nevertheless, the extremely high sensitivity of spontaneous Raman scattering with the whole unresolved Q-band of Raman scattering recorded under conditions of absence of incoherent stray light is a strong argument in favor of the application of spontaneous Raman scattering in all cases whenever possible.

However, the situation changes sharply as soon as other factors that exist in real experiments come into play, and first of all noncoherent stray light due to scattering of the pump light by dust, luminescence (including chemiluminescence), thermal emission from the gas and from heated particles of soot, dust, etc. Under these conditions, as we have already stressed repeatedly, the sensitivity of spontaneous Raman scattering

falls sharply by many orders of magnitude as compared with the sensitivity of the coherent methods. Figure 18 illustrates this situation; the graph shows the calculated variation of the detection power of the various methods normalized to "ideal" conditions as a function of the spectral brilliance of the background noncoherent emission (in photons/steradian \cdot cm⁻¹).

Among the cited sources of noncoherent stray light, the most serious problem arises from emission from solid particles or other aerosols, which are always present, in particular, in the combustion products of solid or liquid fuel. When acted on by focused laser radiation, these particles can be strongly heated (up to 3500–5000 K) and emit intense thermal radiation in synchrony with the laser pulses. Typical values of the spectral brilliance of this emission amount to 10^6 – 10^9 photons/s \cdot steradian \cdot cm⁻¹.⁸⁷ Under these conditions, as we can see from Fig. 18, the efficiency of spontaneous Raman scattering is infinitesimal, whereas the coherent methods still possess a sensitivity close to the quantum limit.

Thus the coherent methods have an overwhelming advantage over spontaneous Raman scattering, at least in two respects—in sensitivity of determining small concentrations of impurity molecules under conditions of strong noncoherent emission from the gas under study, and in spectral resolution. In addition, they have a considerably greater speed of action and spatial resolution.

CONCLUSION

The material presented in this review indicates the great potentialities of the nonlinear-optical methods of Raman spectroscopy in gas analysis. Primarily this pertains to active Raman spectroscopy, with which unique data have already been obtained in the study of flames, discharges, aerodynamic flows, and reactive jets. CARS and the other nonlinear optical methods make it possible to measure exactly, with a high signal-to-noise ratio and great speed of action, the spatial distribution of concentration, temperature, and pressure of various components of gas mixtures. The promising results of applying CARS for these purposes are ensured by a number of its substantial advantages over other optical methods of nonperturbing gas analysis, and mainly over spontaneous Raman spectroscopy.

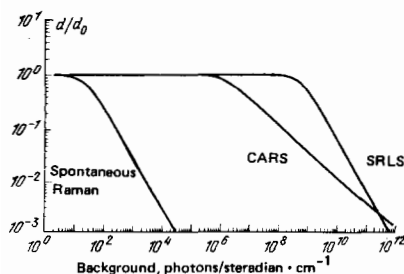


FIG. 18. Relative detecting power of the spontaneous Raman, CARS, and SRLS methods with respect to the level of background stray light. Here d_0 is the detecting power of the corresponding methods in the absence of the background stray light.

The high intensity of the anti-Stokes signal of CARS and the speed of action of the order of the duration of the exciting laser pulse (in the range 10^{-12} – 10^{-8} s) place this method ahead of the competition in the study of fast and explosive processes, including cases in which components at low concentrations are of interest. The restrictions on the sensitivity of CARS in determining concentrations of impurities that are imposed by the existence of the nondispersive coherent "background" in active spectra have currently been practically eliminated, owing to the development of a set of new modifications of the method, such as polarization CARS and modulation methods of Raman spectroscopy. The sensitivity of CARS already exceeds that of spontaneous Raman scattering in the detection of trace impurities for most gases by a factor of 10–100, while when the gas is dusty or when other solid particles contaminate the gas, this advantage of CARS becomes overwhelming.

The advantage of CARS and allied nonlinear-optical schemes over other optical methods of vibrational-rotational spectroscopy with respect to spectral resolution are great. This is especially important in studying the Raman spectra of molecules in the gas phase, in which all the spectral lines are discrete and extremely narrow.

Although it would be incorrect to assert that active Raman spectroscopy is capable of fully replacing other optical methods of gas analysis, we can assuredly say that its employment together with other methods of nonperturbing monitoring of gaseous media substantially expands the potentialities of studying the processes that occur in them. What we have said pertains in the highest degree to studying processes in reactive and rocket motors, in high-power gas lasers, in apparatus for laser separation of isotopes, in kinetics of processes of combustion and explosion, and in processes of aerodynamic flow around solid objects.

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