Problems in laser spectroscopy

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The introductory section of the review lists the main problems which can be solved by laser spectroscopy methods: 1) achievement of the ultimate resolving power; 2) suppression of the Doppler broadening in the gaseous phase; 3) attainment of the ultimate sensitivity in spectroscopic analysis of atoms and molecules; 4) investigation of the spectra and relaxation originating from excited states; 5) remote spectroscopic analysis; 6) local spectroscopic analysis. This is followed by a section which presents the current status of tunable lasers, including dye solution, semiconductor, and high-pressure molecular gas lasers, parametric oscillators, and spin-flip lasers; nonlinear frequency conversion methods are also considered. Next, a more detailed analysis is made of the following types of laser spectroscopy: 1) linear spectroscopy (external absorption, intraresonator absorption, optoacoustic, and fluorescence methods, and a comparison of these methods); 2) nonlinear spectroscopy free of the Doppler broadening (absorption saturation, two-photon, and particle "trapping" method; a comparison of the sensitivity and resolution of these methods; new spectroscopic information; precision spectroscopy); 3) Raman (spontaneous, inverse, and active) spectroscopy; 4) two-photon absorption spectroscopy; 5) selective detection of small amounts of atoms and molecules (local and remote detection); spectroscopy of excited states, high states of atoms, and vibrational states of molecules; picosecond laser spectroscopy of excited molecules).

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CONTENTS

1. INTRODUCTION. MAIN PROBLEMS

The development of lasers, which are sources of coherent optical radiation available for extensive use in science and technology, has opened up an unusually wide range of applications of light. Many branches of science and technology are now growing on the basis of utilization of the great potentialities of coherent light. Optical spectroscopy is no exception. We can say that essentially a new branch of research has been established and it lies at the interface between quantum electronics and optical spectroscopy, and this branch is usually called laser spectroscopy. The strength of this branch can be judged by regular international conferences at which laser spectroscopy problems are being discussed.[1-4]

Initially, serious utilization of lasers in spectroscopy was stimulated by the development of sufficiently powerful lasers operating in the pulse regime or continuously at some fixed frequencies in the visible range. These lasers are being used successfully in the excitation of the Raman scattering spectra. The next, and probably fundamental, stage in the growth of this spectroscopy was the development of tunable lasers. The use of such lasers has had an extremely powerful influence on optical spectroscopy, altering radically its methods and capabilities. The revolution taking place in optical spectroscopy due to the use of tunable lasers can be compared with the influence of the klystron on radiofrequency spectroscopy.

Laser spectroscopy has made it possible to solve or begin solving several basic problems which have been essentially outside the scope of the classical spectroscopy. These problems include the following.

1) The attainment of ultimate resolution governed not by the instrumental width of the spectroscopic instrument but by the broadening of the spectral lines of matter. This is particularly important in the infrared spectroscopy of gases, in which a resolution of the order of 0.01 cm^{-1} has been achieved only for unique systems and the resolution of the best commercial instruments is 0.1 cm^{-1}, which is 10^2 times higher than the Doppler width of spectral lines.

2) Suppression of the Doppler broadening in the spectroscopy of atoms and molecules in the gaseous phase. The highly coherent laser light is the basis of the nonlinear spectroscopy methods which can be used to study the structure of spectral lines normally masked by the Doppler broadening resulting from the thermal motion of particles.[5,6] A resolution of about 10^{10} has been

achieved experimentally and methods have been suggested for achieving a resolution down to the natural width of molecular transitions.

3) Attainment of the ultimate sensitivity in spectroscopic analysis of atoms and molecules. Laser radiation can now be used to record the presence of about 10^2 atoms/cm^3 (fluorescence of Na vapor, excited by a tunable visible laser[7]) or 10^{10} atoms/cm^3 (detection of absorption by a tunable infrared laser[8,9]). Methods have been suggested for laser detection of individual atoms and molecules[10] and for achieving the sensitivity available in the best mass spectrometers. However, in contrast to the mass spectroscopy methods, the laser spectroscopy techniques make it possible to detect not only the type of particle but also its quantum (electronic, vibrational, rotational) state.[11]

4) Investigation of spectra and relaxation originating from excited states of atoms and molecules, i.e., the kinetic spectroscopy of excited states. Laser radiation makes it possible to excite selectively to any quantum state a considerable number of atoms and molecules and to follow the ways in which they relax to the ground state[12] or to investigate quantum transitions between excited states. Ultrashort light pulses make it possible to measure directly the relaxation times of electronically and vibrationally excited molecules in condensed media and to obtain directly information on picosecond processes of excitation transfer and relaxation in molecules.[13]

5) Remote spectroscopic analysis. Directional coherent radiation pulses can be used to study Raman and resonance scattering of atoms and molecules, and to excite fluorescence at considerable distances (up to hundreds of kilometers[14]) from a laser and to obtain information on the atomic and molecular composition. These methods are exceptionally important in the current studies of the atmosphere and pollution of the environment.

6) Local spectroscopic analysis. The focusing of laser radiation makes it possible to carry out a spectroscopic analysis of microscopic amounts of matter localized in small volumes right down to λ^3 (λ is the radiation wavelength). This has been used successfully in local emission spectroscopy.[15] However, potential applications of local spectroscopic analysis are much wider and extend to medicine and biology.

It must be stressed specially that the use of lasers widens spectroscopy in a natural manner beyond the traditional studies of the composition and structure of matter. Laser radiation can be utilized in conjunction with the selective absorption of light by matter to interact selectively with matter so as to alter its composition and properties.[16] This is sometimes called the *active laser spectroscopy*. In a wider sense, laser spectroscopy is a necessary intermediate stage in practical and fundamental applications of coherent light in chemistry, biology, and other subjects.

The optical spectra of atoms and molecules are influenced by the properties of the nuclei (mass, excita-

tion energy, spin) manifested by the isotopic, hyperfine, and isomeric structures of spectral lines. Very-high-resolution laser spectroscopy makes it possible to measure these effects with high precision. Moreover, many ideas of the nonlinear laser spectroscopy free of the Doppler broadening can be applied to γ-ray transitions in nuclei. In principle, it should be quite feasible to act on optical transitions in atoms and molecules and thus alter the spectral γ-ray lines (absorption) and, in particular, perform γ-ray spectroscopy of nuclei in a gas free of the Doppler broadening.[17] This is a new subject of research at the interface between lasers and nuclear spectroscopy and it is sometimes called laser-nuclear spectroscopy.[18]

In the present review, we shall consider briefly all these laser spectroscopy problems and the most important methods and experiments. The main instrument in the growth of laser spectroscopy methods is the tunable laser. Therefore, it is appropriate to begin this review by considering the current status of tunable lasers.

2. TUNABLE LASERS

Three basically different methods are used to tune lasers: these methods can be employed as the basis of the following classification.

1) Lasers with a wide gain profile and tunable along it in a narrow range of minimal resonator losses. Three important classes of such lasers have been developed successfully and they have solid (semiconductors, activated glasses), liquid (dyes), or gaseous (high-pressure molecular gases) active media. A selective element ensuring minimum losses at a given frequency can be a dispersive resonator or a tunable narrow-band filter.

2) Lasers with a narrow but frequency-tunable gain profile. This method was used, for example, in the first tunable gas lasers based on the Zeeman effect but it has not become popular because of the narrow tuning range. Later, two effective methods for obtaining narrow tunable gain profiles were discovered: one was the parametric oscillation method[19,20] and the other the method of stimulated scattering in a semiconductor subjected to a magnetic field.[21] Both these methods are based on the nonlinear conversion of laser radiation but, in contrast to the generation of sum and difference frequencies, they provide means for laser generation at a tunable frequency.

3) Lasers based on nonlinear frequency conversion (generation of sum and difference frequencies in nonlinear materials). This method is usually employed in combination with one of the methods mentioned under 1) or 2) above so as to extend the frequency tuning range.

A. Dye solution lasers

Dye lasers are the widest class of tunable lasers. In these lasers, the dye molecules are pumped optically from the ground state to an excited electronic singlet state. The high density of the vibrational–rotational levels of complex molecules and the considerable
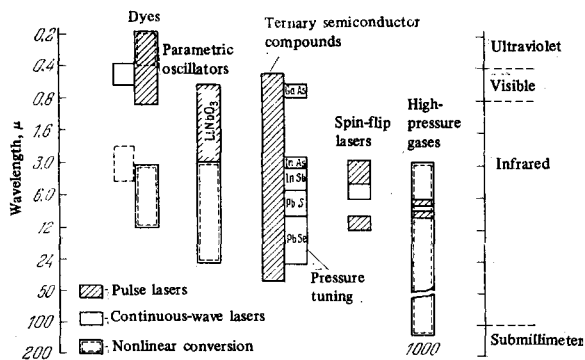
FIG. 1. Tuning ranges of the main classes of tunable lasers.

broadening of these levels in solutions make the gain profiles fairly wide (usually amounting to several hundreds of angstroms). Stimulated emission has already been obtained from a very large number (several hundred) of molecules and these belong to several families.[22-24] They allow us to generate stimulated radiation at any wavelength from 0.34 to 1.2 μ (Fig. 1). Usually, one dye can be frequency-tuned over a range of several hundreds of angstroms and this range may be shifted by a small amount if the concentration and type of solvent is varied. In some cases, the tuning range available from one dye can be extended to 1500 Å.[25] An important family of lasers are scintillators emitting in the ultraviolet range,[26] which can be used to extend the range toward shorter wavelengths, and the recently discovered dye vapor lasers.[27,28]

Very recently, a new type of tunable laser was developed: this laser is pumped similarly to cw tunable dye lasers, but it emits in the infrared range. This is the cw laser utilizing F centers in a KCl : Li crystal pumped by krypton laser radiation.[29] Its tuning range is 2.6–2.8 μ. This type of tunable laser is also promising for spectroscopic applications.[30]

B. Semiconductor lasers

Semiconductor lasers are another important class of tunable lasers with wide gain profiles. Amplification and stimulated emission occur as a result of interband transitions when electrons are injected into the conduction band by an electric current (diode lasers), optical pumping, or bombardment with a beam of fast electrons.[31] Although the best tunability is available from the injection diode lasers, the semiconductor lasers pumped by other methods are also promising.

The width of a gain profile of a semiconductor laser usually ranges from a few tens to a few hundreds of reciprocal centimeters. However, it should be noted that amplification can be obtained at any wavelength ranging from 5000 Å to 30 μ and this can be done by varying the composition of binary and ternary semiconductor compounds.[32] Figure 1 shows the regions in which amplification can be obtained in several semiconductor compounds. Almost all the injection lasers operating in the pulse regime have to be cooled to 77 °K and those emitting continuously have to be kept at temperatures of 4 °K or lower. The exception to

this rule is represented by the $GaAs_{1-x}P_x$ heterojunction lasers,[33] which can operate continuously even at room temperature.

The emission frequency of a semiconductor laser can be tuned within a narrow range (fine tuning) by altering the current, external magnetic field, temperature, or pressure. Narrow spectral intervals are usually scanned by varying the current. External agencies, such as a strong pressure or a magnetic field, can be used to extend considerably the gain profile of a semiconductor laser with a fixed composition. Such coarse tuning enables wide spectral intervals to be covered and makes it possible to attain a high resolution when used in combination with the fine tuning. Variation of pressure up to 15 kbar, which is quite feasible in a compact liquid high-pressure chamber, can be used to obtain stimulated emission at any frequency in the infrared range with just three or four semiconductor lasers (see the review in Ref. 34).

C. High-pressure molecular gas lasers

High-pressure molecular gas lasers can be used to obtain frequency-tunable radiation in some parts of the infrared range and the output power of such lasers is relatively high. A wide gain profile is due to the overlap of neighboring rotational–vibrational lines which results from the collisional line broadening when the gas pressure is increased.[35] A pressure of the order of 10 atm is sufficient for a considerable overlap of the neighboring gain lines of the CO_2 molecule. Compressed molecular gases are usually pumped by an electric discharge in a gas preionized by electron-beam bombardment[36] or by ultraviolet irradiation.[37] Figure 2 shows the tuning characteristics of a high-pressure electron-beam-controlled CO_2 laser with a line width 0.01 cm^{-1}, described in[38]. In contrast to the semiconductor lasers, the output power of the high-pressure gas lasers is very high so that one can use
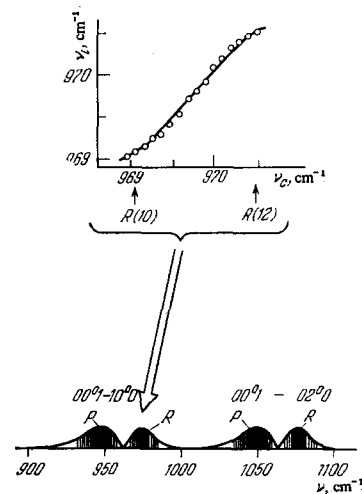

FIG. 2. Tuning characteristics of a high-pressure CO_2 laser. The tuning range is shown shaded in the lower part of the figure. The upper part gives an example of continuous frequency tuning between centers of two rotational–vibrational lines.[38]

V. S. Letokhov

effectively the nonlinear optics methods in converting the emission frequencies of these lasers and covering the whole of the infrared region. The high output power of infrared tunable gas lasers makes it possible to investigate nonlinear effects in the molecules themselves by, for example, selective excitation and dissociation.

D. Parametric oscillators

Parametric oscillators are based on the nonlinear interaction between two intense light waves (ω_1, k_1) and (ω_3, k_3) in a nonlinear material, which amplifies a light wave (ω_2, k_2), whose frequency and wave vector are related by the laws of conservation of energy and momentum to the corresponding parameters of the original two waves: $\omega_1 + \omega_2 = \omega_3$, $k_1 + k_2 = k_3$. The tuning is obtained because at a fixed frequency (say, ω_3) the point of its "splitting" into frequencies ω_1 and ω_2 depends on the phase-matching condition $k_1 + k_2 = k_3$, i.e., it depends on the refractive indices at these frequencies. If the orientation or temperature of an anisotropic crystal is varied, this "splitting" point can be frequency-tuned (see the review in Ref. 39). For example, variation of the temperature of an $LiNbO_3$ parametric oscillator by 200 °K makes it possible to obtain a tuning range from 0.6 to 3.7 μ if the oscillator is pumped with suitable radiation of a shorter wavelength. The available nonlinear crystals can be used in constructing parametric oscillators operating in a very wide range of wavelengths (from visible to far infrared).[40] For example, a CdSe crystal pumped with a $CaF_2 : Dy^{2+}$ laser can generate coherent radiation in the intervals 2.8–3.8 and 8–14 μ.[41]

The parametric oscillation method is very convenient in the generation of picosecond tunable-frequency radiation pulses, particularly in the infrared range. The first successful experiments carried out in[42] demonstrated the feasibility of constructing simple parametric traveling-wave oscillators operating in the 1–10 μ range and generating pulses about 10 psec long when a nonlinear crystal was pumped with picosecond pulses generated by, for example, a neodymium-glass laser. Such a tunable laser is very suitable for picosecond spectroscopy of the vibrational states of molecules in condensed media.

E. Stimulated spin-flip lasers

Stimulated spin-flip lasers are based on the stimulated Raman scattering of laser radiation by conduction electrons in a semiconductor subjected to a magnetic field. This field splits the Landau level of an electron in the conduction band into two sublevels with spin orientations parallel and antiparallel to the magnetic field. The separation between these sublevels is $\Delta\omega_S = g\mu_B H$, where H is the magnetic field, μ_B is the Bohr magneton, and g is the spectroscopic splitting factor of an electron in the conduction band. Stimulated scattering accompanied by the spin flip of an electron occurs in a strong infrared field; this produces the Stokes shift so that $\omega_{sc} = \omega_l - \Delta\omega_S$. The Stokes shift is tunable by a magnetic field. Stimulated spin-flip scattering was observed in an InSb crystal with a given electron den-

sity cooled to about 30 °K and pumped with pulse CO_2 or cw CO laser radiation.[43,44] The use of other semiconductor materials and pump lasers should make it possible to cover completely the whole infrared range with this type of tunable laser, which differs from the others because of the electronic control of the emission frequency.

F. Nonlinear frequency conversion

Radiation of frequency ω_2 emitted by a tunable laser can be mixed with radiation of fixed frequency ω_1 emitted by another laser and, in this way, a tunable radiation of shorter wavelengths can be obtained at the sum frequency $|\omega_1 + \omega_2|$ and at longer wavelengths at the difference frequency $|\omega_1 - \omega_2|$. This method is important because it provides means for the mastering of those parts of the spectrum where no tunable lasers are available (far infrared and submillimeter range, ultraviolet wavelengths) and, secondly, it can be used to extend the tuning range of lasers of a given type which is usually not wider than one octave.

The difference-frequency generation provides an effective means for mastering the far infrared range right up to the millimeter wavelengths. For example, mixing the radiation of two pulse CO_2 lasers, one of which emits radiation which is discretely tunable from one rotational-vibrational line to another, we can generate difference-frequency wavelengths ranging from 70 μ to 1 mm with an output power of 1 to 10^{-4} W.[45]

The sum-frequency generation can be used to master the ultraviolet range between 3400 and 2000 Å, where there is as yet no dye laser. It is usual to double the emission frequency of a tunable dye laser or to sum the emission frequency of a dye laser with high-power radiation of the second harmonic of a solid-state laser. The available nonlinear crystals make it possible to extend the range at least up to 2100 Å. However, one would expect the use of nonlinear quasiresonance effects in metal vapors[46] to provide means for extending this range to even shorter wavelengths by nonlinear optics methods and, which is particularly important, to generate efficiently higher harmonics.

Another promising method for the wavelength range from 1600 to 3400 Å is based on the optical pumping of suitable media with high-power 1550 Å radiation emitted by an H_2 laser,[47] which is capable of megawatt output powers in the form of short pulses ($< 10^{-9}$ sec) emitted at a high repetition frequency; the efficiency of this laser is up to 0.5%. This approach should make it possible to construct simple tunable lasers emitting in the above range, just as the pulse N_2 laser emitting at 3371 Å has made it possible to cover the range of wavelengths longer than 3500 Å by pumping a dye laser.

Thus, the main methods have now been mastered and the principal classes of lasers have been constructed for tuning the emission wavelengths from the ultraviolet to the submillimeter range. Some of these lasers cover frequency intervals amounting to two or three octaves, but the majority are tunable within one octave or even just by 5–10% of the emission frequency. The

use of various active media in one type of laser or even in one particular system makes it possible to extend the tuning range of one laser to at least one octave.

Practically all the tunable lasers are capable of emitting single-mode narrow-band radiation and the technical means ensuring such emission have been found. Line widths in the range from 1 kHz to 1 MHz characterize continuous emission. In the case of pulse lasers, the spectral widths are governed by the reciprocal of the pulse duration: 10–30 MHz for pulses 30–10 nsec long. Consequently, even in the case of pulse lasers, the emission line width is less than the Doppler width of the narrow absorption lines of gases and far less than the line width of gases at atmospheric pressure. This makes it possible to achieve the ultimate resolution in the determination of the absorption spectra of matter.

In spectroscopic applications, an important parameter is the radiation power per unit frequency interval, i.e., the spectral density of the emitted radiation. High values of this density can be achieved because the emission lines of lasers are narrow. For example, in the case of a cw injection laser with an output power of just 10^{-4}–10^{-5} W, the spectral density of the output power is 10^{-9} W/Hz, which corresponds to the emission from a black body of size amounting to several meters and kept at a temperature of 2000 °K. The high spectral density and the spatial coherence of the laser radiation ensure a high spectral brightness. For example, even in the case of a low-power cw laser diode, the spectral brightness is at least 10^{-5} W $\cdot$ cm^{-2} $\cdot$ sr^{-1} $\cdot$ Hz^{-1}, which is many orders of magnitude higher than the spectral brightness of thermal infrared radiation sources. For example, a black body kept at 2000 °K is characterized by a spectral brightness of 2×10^{-14} W $\cdot$ cm^{-2} $\cdot$ sr^{-1} $\cdot$ Hz^{-1} at $\lambda = 10$ μ. This means that, even if low-power lasers are used in high-resolution linear absorption spectroscopy, the signal/noise ratio of a spectrometer can be improved by many orders of magnitude compared with the ratio for conventional light sources.

We shall conclude this optimistic review of the status of tunable lasers by the caution that many of these lasers are not yet available to the majority of laboratories where their potentialities can be utilized. Therefore, the majority of the experiments described below was carried out by the researchers who developed these lasers and should be regarded simply as illustrations of the capabilities of these lasers. It will be several years before tunable lasers are used extensively in research laboratories.

3. LINEAR LASER SPECTROSCOPY

A. Principal methods

Three methods are used most widely in spectroscopic investigations of matter with the aid of tunable lasers, i.e., without conventional spectroscopic instruments performing spectral resolution of the radiation. In the simplest case, measurements are made of the dependence of the transmitted energy on the tunable laser wavelength. This is the *external absorption* method, which is particularly convenient for the determination of fairly strong absorption lines when the absorbed energy represents a considerable proportion of the incident energy, for example, more than 1%. If the absorbed energy is only a very small proportion of the incident energy, it is frequently more convenient to record directly the absorbed energy. For example, in the spectroscopy of absorbing gases, we can use the change in the temperature and pressure of a gas which results from the absorption, i.e., we can utilize the *optoacoustic* effect for recording the absorbed energy. In some cases, the absorption is accompanied by re-emission of the radiation by the excited particles, i.e., fluorescence is observed. Measurements of the intensity of this fluorescence as a function of the wavelength of the exciting laser radiation is the basis of the *fluorescence* method in laser spectroscopy, which is also highly sensitive. We shall now consider briefly each of these linear spectroscopy methods. The linearity means that the intensity of the laser radiation is well below the threshold of the onset of the nonlinear effects due to changes in the level populations (saturation effect) and many-photon transitions.

B. External absorption method

The advantages of the determination of the absorption spectra with tunable lasers are particularly striking in the case of the rotational–vibrational lines of molecules in the infrared range. The resolution of even very good spectrometers is much greater than the absorption line width of gases at low pressures (less than several torr), when the broadening is due to the Doppler effect. Therefore, the structure of these lines is lost within the resolution interval. This can be illustrated by the example of the determination of the absorption spectrum of the SF_6 molecule with a very-high-quality diffraction-grating spectrometer (resolution 0.07 cm^{-1})[48] and a laser spectrometer with a tunable diode[49] (Fig. 3). The sulfur hexafluoride molecule has an exceptionally complex infrared spectrum, which cannot be resolved in the region of 950 cm^{-1} even with a very-high-quality spectrometer but it is easily resolved with a tunable laser.

Thus, a laser absorption spectrometer makes it possible to determine directly the profiles of narrow absorption lines of atoms and molecules in gases. This provides an opportunity for investigating the influence of collisions on the line profiles of moving particles. Experiments of this kind revealed, in addition to the expected collisional broadening of the absorption lines, nontrivial collisional narrowing of spectral lines. This was first found in studies of the $\lambda = 5$ μ absorption lines of the H_2O molecule in a buffer gas (Xe, Ar, N_2).[50] This is the optical analog of the narrowing due to the Dicke effect,[51] which is well known in the radio-frequency range. A practical application is the determination of the molecular masses from the direct measurements of the Doppler broadening, provided the composition of the molecular gas is known. This is important in the identification of molecular impurities in the environment by laser spectroscopy.
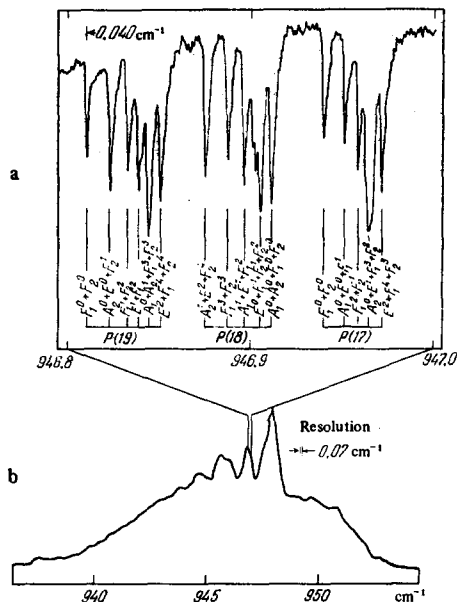
FIG. 3. Infrared spectrum of the ν_3 band of SF_6, determined using a classical high-quality infrared spectrometer[48] (a) and a part of the infrared transmission spectrum determined with a tunable injection laser[49] (b).

The ultimate sensitivity of the laser absorption method[52] corresponds to the detection of just 10^2 atoms. In the case of the rotational–vibrational transitions of the molecules and heterodyne reception on the basis of photoconductivity, the minimum detectable number of molecules is 10^8–10^9. The lower sensitivity in the case of molecules is due to the slower relaxation of the excited particles and the relatively low populations of the levels involved in these transitions. Nevertheless, the absorption laser spectroscopy methods make it possible to detect relative concentrations of molecules of 10^{-9} in a volume of 1 cm^3 when the gas pressure is several tens of torr.

Thus, the external absorption laser spectroscopy has two main advantages over the conventional spectroscopy:

1) it makes it possible to attain the ultimate resolution governed by the broadening of absorption lines in gases and not by the instrumental transfer function;

2) it makes it possible to record extremely weak absorption lines, so that either the amount of matter necessary for the determination of the intense lines in the spectra can be very small or it is possible to detect exceptionally weak lines using the same amount of matter as in the conventional absorption spectroscopy.

In this connection, it is worth drawing attention to the relative ease of the detection and measurement of the forbidden molecular transitions by laser spectroscopy methods. For example, Herzberg[53] detected forbidden rotational–vibrational lines of the homonuclear molecule H_2 in the 11 300–12 400 Å range (2–0 band) and in the 8000–8600 Å range (3–0 band) using optical paths from 10 to 50 km/atm. The use of a laser in the measurements of the absorption at the same lines

makes it possible to reduce the optical paths by a factor of a million.

C. Intraresonator absorption method

A very efficient highly sensitive laser method for the detection of weak absorption lines involves placing, inside the resonator of a multimode laser with a wide gain line, of a medium which absorbs weakly within this gain line. This method was proposed and demonstrated by Pakhomycheva et al.[54] using a pulse neodymium-glass laser. When a cell is placed inside the resonator, the weak absorption at the various frequencies results in a redistribution of the intensities of the emitted modes. Those modes which lie within weak absorption lines are suppressed, i.e., selective mode quenching takes place. This produces sharp peaks in the emission spectrum of the laser and such peaks are readily detected with a conventional spectrograph. This method can be applied to lasers with wide gain lines within which a very large number of axial modes can be concentrated. It is known that pulse and cw lasers with wide gain lines (such as neodymium-glass and dye lasers) emit a very large number (10^3–10^5) of axial modes unless special measures are taken to narrow down the spectrum. In the pulse regime, a large number of axial modes is emitted practically independent of one another. In the cw or quasicontinuous emission, a large number of axial modes coexists either because of the inhomogeneous broadening of the gain line or because of the spatially inhomogeneous distribution between modes with different field distributions and the amplifying medium, or due to the simultaneous action of both effects.

In the case of a pulse laser, a weak absorption line can be detected if light is weakened by a factor e as a result of repeated transits through the absorption cell in the resonator during the stimulated emission time t_{st}. The sensitivity of the intraresonator cell method is higher than the sensitivity of the single-pass measurement of the absorption coefficient $\varkappa_0$ outside the resonator by the factor

$$S = \frac{\varkappa_0}{\varkappa_{\text{intrares}}} = \frac{ct_{st}}{L}, \tag{3.1}$$

where c is the velocity of light and L is the resonator length. For example, a free-oscillation neodymium-glass laser ($t_{st} \approx 10^{-3}$ sec) can be used to detect extremely weak absorption lines of molecules (NH_3, HN_3, CO_2, C_2H_2, C_2HD, NCN, H_2O, etc.) due to combination vibrational–rotational transitions in the 9380–9480 cm^{-1} range characterized by absorption coefficients of the order of 10^{-7} cm^{-1}, i.e., the use of this laser ensures an increase in the sensitivity by a factor of $S \approx 10^5$.[55]

An extremely high sensitivity can be achieved using a cw laser with a smooth emission spectrum. For example, in the first experiments carried out using a cw dye laser, an increase in the sensitivity of the recording of absorption lines of the I_2 molecule was a factor of 10^5.[56] Figure 4 shows the spectrum of weak absorption lines of air in the 5800–6200 Å range, obtained under laboratory conditions using a cw dye laser.[57]
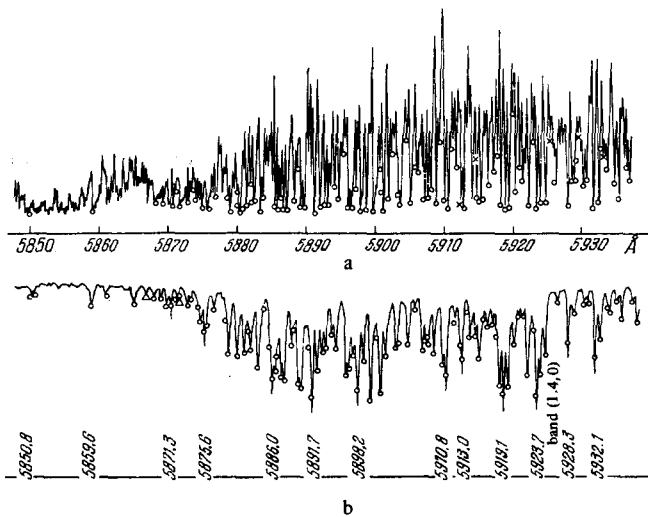
FIG. 4. Spectrum of very weak absorption lines of air in the red region obtained by the intraresonator absorption method under laboratory conditions[57] (a) and by measuring the atmospheric transmission above an ocean bay over a path of 16 km[58] (b).

For comparison, this figure also gives the absorption spectrum of the atmosphere obtained in the same range using an optical path of 16 km above the surface of the sea. This is a clear demonstration of the effectiveness of the intraresonator absorption cell method. The sensitivity in the cw case is limited probably because of the contribution of the spontaneous radiation to the oscillation modes, which makes it impossible to quench completely the relevant modes under weak absorption conditions[59] or it may be due to the quenching of the cw emission of fixed modes caused by technological disturbances in the laser resonator.[57] In the latter case, the sensitivity is given by Eq. (3.1), where t_{st} should be understood to be the average emission time of fixed modes.

At first sight, it seems that the intraresonator absorption method would be difficult to use in quantitative analysis. However, this is not true. It is shown in[55] that, if the laser emission spectrum is recorded at two successive moments t and $t + \Delta \tau$, at which the depth of a dip in the spectrum differs by a factor e, we can quite accurately determine the absolute selective absorption

$$\varkappa_{sel} = (c \Delta \tau)^{-1}. \tag{3.2}$$

Finally, the intraresonator cell method is exceptionally promising for the recording of weak absorption (and gain) lines of short-lived (10^{-3}–10^{-6} sec) products of chemical reactions, radicals, and unstable molecules.

D. Optoacoustic method

The optoacoustic linear spectroscopy method is based on the effect discovered by Bell, Tyndall, and Röntgen in the last century.[60] The effect is manifested by gas-pressure pulsations in a closed chamber as a result of absorption of infrared radiation modulated at an acoustic

frequency. The effect was subsequently investigated thoroughly by Veǐngerov[61] and used by him to construct a gas analyzer suitable for qualitative and quantitative analysis of gas mixtures. The method was improved considerably by Kreuzer,[62] who was the first to replace a monochromatic thermal radiation source with an infrared He–Ne laser whose emission line at 3.39 μ coincided with the absorption line of CH_4. The very high spectral density of the laser radiation power made it possible to increase the sensitivity of detection of the absorption lines by several orders of magnitude.

When the laser radiation frequency coincides with the frequency of an absorption line of a gas, for example, with the line of impurity molecules in a gas, these molecules are excited. They return to the original state by:

1) nonradiative vibrational–translational relaxation characterized by a time constant τ_{V-T} and accompanied by the heating of the gas; 2) radiative relaxation with a time constant τ_{rad}. The inequality $\tau_{V-T} \ll \tau_{rad}$ is satisfied by the majority of molecules at pressures above 1 Torr and, consequently, the absorbed energy is converted mainly into heat and causes changes in the gas pressure. These changes bend a sensitive membrane which is part of a capacitor microphone.

The sensitivity of a capacitor microphone is sufficient to detect reliably absorbed powers P_{abs} of the order of 10^{-8}–10^{-9} W in a path $l = 10$ cm long when the pass band of the recording system is $B = 1$ Hz.[62] The physical sensitivity threshold is set by the Brownian noise of the microphone membrane resulting from the thermal motion of the gas particles. If the microphone is constructed carefully, P_{abs} exceeds this limit by about one or two orders of magnitude.[62] The high sensitivity of the optoacoustic method, in combination with a tunable infrared laser, makes it possible to detect very low concentrations of molecular pollutants in air. For example, the presence of the NO and H_2O molecules was detected in a concentration of 10^9 cm^{-3} at an altitude of 28 km using a cw spin-flip laser (1820 cm^{-1}) in a spectrometer suspended from a stratospheric balloon.[63]

When such very weak absorption lines are being detected, certain limitations become important and these include weak absorption in the wings of distant strong absorption lines, the presence of unavoidable molecular absorbing impurities in the cell, and the optoacoustic signal due to the cell windows which also absorb weakly. The last effect can be eliminated using a pulse laser and sending a short radiation pulse to a cell and detecting the optoacoustic signal only from the central part of the cell. In the pulse regime without accumulation of data, it is quite feasible to reach a sensitivity of absorption detection of the order of $\varkappa_{min} \approx 10^{-9}$ cm^{-1} using pulses of 1 J energy.[64] For example, a pulse HF laser emitting at $\lambda = 2.7$ μ was used to detect the presence of the HF, NO, and CO_2 molecules when their relative concentration was 10^{-6} in air. Figure 5 shows the experimentally determined dependence of the detectable absorption coefficient on the HF laser pulse energy.[64] When the pulse energy is increased, the transition becomes saturated and the sen-
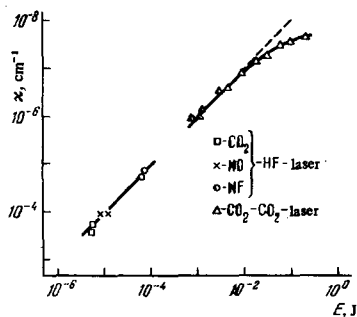
FIG. 5. Dependence of the sensitivity of the pulse acoustooptic detection of the absorption in the HF, NO, and CO_2 molecules on the energy of a CO_2 pulse laser.[64,65]

sitivity limit is reached. A dependence of this kind, obtained in[65] for a CO_2 laser and the CO_2 molecule, is included in Fig. 5. It should be noted that determination of this dependence is a convenient and simple method for measuring the saturation energy of weak molecular transitions.[65]

The optoacoustic method has been applied so far to infrared vibrational transitions in molecules. This is dictated by the requirement that the excitation energy be converted into heat. However, the method can also be applied in the visible range if high vibrational overtones of molecules (such as H_2, HD, HF, etc.) are excited. The method can likewise be used in the spectroscopy of weak absorption lines of condensed media, particularly in the infrared spectroscopy of the surface states.

E. Fluorescence method

The fluorescence method is based on the recording of the energy absorbed from a laser beam and converted into the fluorescence of particles excited in a sample. It is applicable to quantum transitions in atoms and molecules accompanied by the radiative decay of the excited states. In the external absorption method, the eventual fate of the particles excited by absorption is of no importance, whereas, in the optoacoustic method, the excitation of the majority of the particles should be converted nonradiatively into heat and, in the fluorescence method, the relaxation channel should be mainly radiative. In this sense, the fluorescence method is complementary to the optoacoustic method and, in principle, the two methods taken together can cover any type of transition. The sensitivity of the fluorescence method is extremely high. It is reduced by about two or three orders of magnitude by the low quantum efficiency of photodetectors and because of the geometric factor; this reduction may be compensated by multiple absorption and repeated reemission of photons during the recording time. Clearly, if there are no other factors that can limit the sensitivity, the fluorescence method should, in principle, ensure the attainment of the sensitivity limit corresponding to the detection of one particle in a quantum state in the investigated medium.

The excitation of the atomic fluorescence by laser

radiation has been achieved only for some elements in the periodic table and the absorption lines of these elements lie in the range which is currently accessible to tunable dye lasers. The highest sensitivity ($\sim 10^2$ atoms/cm^3) has been achieved for the Na atoms[7] and this sensitivity is considerably higher than the sensitivity of any other optical detection method. In principle, it should be possible to detect just one atom in a gas at a very low pressure or in an atomic beam and, consequently, it should be possible to follow its trajectory by recording the fluorescence. For example, in a path of 1 cm, an atom should absorb and reemit about 10^4–10^5 photons in 10^{-4} sec and this should be sufficient for the visualization of its trajectory. Naturally, the trajectory will be distorted by the "instrument" (exciting light wave) because of the recoil effect.

The use of the fluorescence method in the detection of simple molecules and radicals is even more promising. The high sensitivity of the method makes it possible to detect the products of chemical reactions occurring in molecular beams.[111] In this case, the sensitivity of the fluorescence method is fully comparable with the sensitivity of the best mass spectrometers but, in contrast to the latter, a laser fluorescence detector is highly selective because it records molecules in a specific rovibronic (electronic–vibrational–rotational) state. For example, Schulz et al.[66] used the fluorescence method to study the inhomogeneous distribution of the energy between the levels of the BaO molecule resulting from the $Ba + O_2 \rightarrow BaO + O$ chemical reaction. Dye laser pulses with far from optimal parameters were used to detect 5×10^4 molecules of BaO in 1 cm^3 at a specific rotational-vibrational level (v, J). The use of much improved cw dye lasers now available should increase the sensitivity by several orders of magnitude.

The method of laser excitation of the fluorescence of particles in a molecular beam is ideal for measurement of microscopic (elementary) rate constants of chemical reactions without averaging over all the states in the equilibrium distribution.[111] Laser radiation can be used as a probe for the detection of the presence of particles in specified quantum states before collisions cause relaxation to the equilibrium distribution. Information obtained in this way can be used to find the proportions of the energy distributed between the rotational, vibrational, and translational degrees of freedom.

The fluorescence method is likely to be very suitable for the detection of the OH radicals. These radicals are very difficult to detect by mass spectrometry because of the overlapping contribution of the OH* mass peak due to the unavoidable presence of the H_2O background. However, the OH radicals can quite easily be detected by laser radiation in the 3000 Å range. This is an important task in atmospheric photochemistry since there have been suggestions that even smaller amounts of OH (10^6–10^8 cm^{-3}) can control the CO $\rightarrow CO_2$ conversion in the terrestrial atmosphere and are an important intermediate product in the chemistry of smogs. A sensitivity of the order of 10^6 cm^{-3} in the detection of the OH radicals was achieved in[67] and the
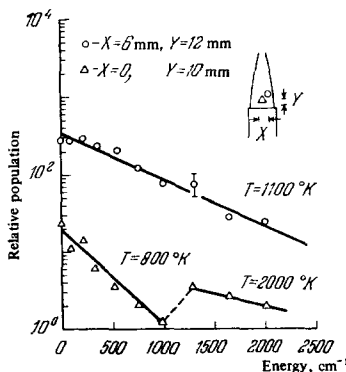
FIG. 6. Dependences of the relative populations of the rotational energy levels of the OH radical in the ground vibronic state on the rotational energy at two different points in a Bunsen burner flame, obtained by the laser fluorescence method.[67]

fluorescence method was used to study the distribution of the populations of OH in the ground electronic state in a Bunsen flame. Figure 6 shows the relative populations at various points in such a flame. We can clearly see that the distribution at some points is not in equilibrium and cannot be described by a single rotational temperature.

In these experiments on the OH radicals, a high spatial resolution was achieved by focusing a laser beam into a spot of 100 μ diameter. This is a very important feature of the laser fluorescence method because it can be used to carry out microfluorescence spectroscopic analysis. This feature is also important in biological applications and can be used, for example, in microfluorescent detection of antibodies.[68].

F. Comparison of methods

None of the linear laser spectroscopy methods discussed above is universal and these methods complement rather than duplicate each other. Table 1 gives the ranges of application of the various methods and their principal characteristics. The widest range is that of the external absorption spectroscopy which covers, in principle, any transitions in atoms and molecules corresponding to the ultraviolet, visible, and infrared parts of the spectrum. However, a shortcoming of this method and of the next two methods is a low spatial resolution (particularly along the beam).

The sensitivity of the external absorption method can be high only if the observation time is sufficiently long, which seriously limits the temporal resolution. The intraresonator absorption method is applicable (so far) only in the ultraviolet and visible range for which lasers with wide gain lines are available. In contrast to the single-pass method of transmission measurement, the intraresonator method can be used to achieve an extremely high sensitivity in a very short time. The optoacoustic method is applicable to molecular transitions in the infrared range accompanied by nonradiative relaxation of the excitation (in the two absorption methods, the type of relaxation is unimportant). The time constant of the optoacoustic method is relatively high because of the slow relaxation of a gas in a cell to its initial state. The sensitivity of the optoacoustic method is comparable with the sensitivity of the absorption method for the same recording time but the optoacoustic method is simpler to use. The fluorescence method has the best characteristics but it is applicable only to transitions with a radiative excitation-relaxation channel, i.e., to electronic transitions in atoms and molecules corresponding to the ultraviolet and visible parts of the spectrum. This method is characterized by a very high spatial resolution right down to λ^3. The ultimate sensitivity representing the detection of one atom or molecule in a given quantum state may be reached in a relatively short observation time. However, if a lower sensitivity is sufficient, one can use a time constant not exceeding 10^{-8} sec. Thus, in the case of allowed electronic transitions in atoms and molecules, the fluorescence method has no equal. However, this does not mean that it satisfies all the requirements of atomic and molecular spectroscopic analysis. The analytic methods should not only be highly sensitive but also highly selective or have a high spectral resolution. The electronic absorption bands of the majority of molecules are similar in the ultraviolet region and, in spite of the high sensitivity, the detection of complex molecules by laser radiation is not yet possible. This problem is discussed in greater detail in Sec. 7.

4. NONLINEAR LASER SPECTROSCOPY FREE OF DOPPLER BROADENING

The restriction of the resolution of optical spectroscopy because of the Doppler effect can be eliminated by

TABLE 1. Comparison of linear laser spectroscopy methods.

Characteristic	External absorption method	Intraresonator absorption method	Optoacoustic method	Fluorescence method
Range of application	Absorption lines of atoms and molecules in ultraviolet, visible, and infrared	Absorption lines of atoms and molecules in visible range	Vibrational–rotational absorption lines of molecules	Electronic transitions of atoms and molecules in ultraviolet and visible range
Spatial resolution	Low	Low	Low	In principle, down to λ^3 (in practice, 10^{-6} cm^{-3})
Sensitivity	Down to 10^2 atoms	10^5 atoms	10^8–10^9 molecules	In principle, down to one atom or molecule in quantum state
Temporal resolution (for above sensitivity)	1 sec	10^{-6} sec	10^{-3} sec	10^{-4} sec (in principle, down to 10^{-9} sec)

applying various methods, developed before the discovery of the laser, and these methods make it possible to study the structure of quantum transitions masked by the Doppler broadening of spectral lines. One of these methods is the atomic or molecular beam technique developed in the thirties and used successfully ever since. In the fifties, a discovery was made of several spectroscopic methods free of the Doppler broadening (radio—optical double resonance method,[69] level crossing method,[70,71] quantum beat method[72,73]) which are applied mainly to atomic transitions in the visible range. The capabilities of each of these methods are discussed in detail in reviews[74-76] published earlier in the present journal.

The development of laser sources of coherent radiation with narrow spectral lines and tunable frequencies has extended considerably the capabilities of all the methods free of the Doppler broadening; however, the most important point is that the laser radiation has made it possible to discover and use widely nonlinear laser spectroscopy methods which, like the method of atomic or molecular beams, are exceptionally effective when applied to any atomic and molecular transitions in a very wide frequency range (ultraviolet, visible, and infrared).

The nonlinear laser spectroscopy methods free of the Doppler broadening can be based on at least three basically different approaches:

1) the saturation spectroscopy, which utilizes the change in the velocity distribution of particles in two levels of a transition due to the action of a coherent light wave[77];

2) the two-photon spectroscopy, which uses two-photon transitions in the field of two waves of identical frequency traveling in opposite directions[78];

3) the spectroscopy of "trapped particles," based on the change in the velocity distribution of particles irrespective of their quantum state, i.e., on the change in the distribution function simultaneously in all quantum levels.[79]

A. Absorption saturation spectroscopy

This method is discussed in sufficient detail in the review[80] and in the monograph.[5] Therefore, we shall give only a quantitative account of the essence of the method and of the information needed for the comparison of all three approaches.

A Doppler-broadened spectral line is essentially a set of a very large number of much narrower spectral lines due to particles (atoms or molecules) traveling at different velocities $\mathbf{v}$. The width of the spectral line of each particle is governed by the homogeneous width 2Γ. A coherent light wave of wave vector $\mathbf{k}$ and frequency ω interacts only with the particles which are in resonance with this wave, i.e., with the particles whose Doppler frequency shift $\mathbf{k} \cdot \mathbf{v}$ compensates exactly the detuning of the field frequency ω from the transition frequency ω_0 of the molecule at rest $(\omega_0 + \mathbf{k} \cdot \mathbf{v} = \omega)$. The excitation of particles with a given velocity alters the
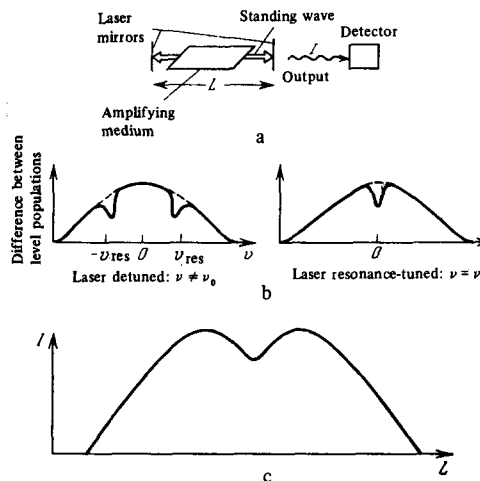

FIG. 7. Formation of a Lamb dip in the emission spectrum of a gas laser. a) Schematic diagram of the apparatus. b) Distribution of the difference between the level populations plotted against the velocity for the case when the field frequency is detuned relative to the central frequency ν_0 and when it is tuned exactly to this frequency $(\nu = \nu_0)$. c) Observed dependence of the output power of a laser on the emission frequency, tuned by varying the resonator length L.

equilibrium distribution of the particle velocities at each of the levels of the transition. A "hole" forms in the distribution of the particles at the lower level because of the loss of particles with $\mathbf{k} \cdot \mathbf{v} = \omega - \omega_0$, whereas the corresponding distribution for the upper level acquires a "peak" due to the same particles. This distorts the Doppler-broadened absorption or emission line. If a Doppler profile is observed collinearly with a light wave saturating the relevant transition, a Bennett hole or dip appears.[81] The width of this hole governs directly the homogeneous width of the transition which may be thousands of times less than the Doppler width.

We shall now consider the effect known as the Lamb dip, used in many experimental studies of the absorption saturation spectroscopy. Let us assume that a standing light wave is interacting with a Doppler-broadened line. Such a wave usually exists inside the laser and it can be represented by a superposition of two waves of identical frequency traveling in opposite directions (Fig. 7). In this case, each of the waves burns out its own hole in the molecular velocity distribution. Since the two traveling light waves are oppositely directed, they produce two holes which are located symmetrically relative to the center of the Doppler gain profile. The laser field acquires energy from two groups of amplifying particles with different velocities. When the laser frequency is tuned to the center of the Doppler gain line, the two holes coincide and the standing wave interacts then with just one group of particles, which causes a resonant fall of the output power of the laser at the center of the gain line. This phenomenon was first discussed by Lamb in 1962[77] in his theory of the gas laser and is now known as the Lamb dip. The Lamb dip was observed experimentally by two groups working independently at the Massa-

TABLE 2. Absorption saturation spectroscopy methods.

Method	First suggested by	First experiment
Lamb dip	Lamb (1967)[77]	Szöke, Javan (1963)[82] McFarlane, Bennett, Lamb (1963)[83]
Inverted Lamb dip	Letokhov (1967)[84] Lee, Skolnick (1967)[85] Lisitsyn, Chebotaev (1967)[86]	Lee, Skolnick (1967)[85] Lisitsyn, Chebotaev (1967)[86]
Dip for opposite weak wave	Letokhov, Chebotaev (1969)[87]	Basov, I. N. and O. N. Kompanets, Letokhov, Nikitin (1969)[88]
Dips for coupled transitions	Schlossberg, Javan (1966)[89]	Schlossberg, Javan (1966)[89]
Particle population resonance (fluorescence intensity dip)	Basov, Letokhov (1968)[90]	Freed, Javan (1970)[91]

chusetts Institute of Technology and Yale University.[82,83]

This spectroscopy changed to a well-developed branch of nonlinear laser spectroscopy because of the discovery of several methods which are summarized in Table 2. Among them, we should mention specially the nonlinearly absorbing cell method,[84-86] i.e., the method for observing the inverted Lamb dip, the method of a probing opposite wave,[87,88] the method for observation of narrow resonances due to transitions coupled to the transition being saturated,[89] and the method for observing narrow intensity resonances of the fluorescence of excited particles.[90,91]

The saturation spectroscopy method has been used in scores of experiments on atoms and molecules in many laboratories. Even a simple listing of these experiments would be impossible in the present review. By way of example of typical information that can be obtained, we give in Fig. 8 the nonlinear absorption spectra of two monoisotopic OsO_4 molecules in the vicinity of several CO_2 laser lines.[92] The width of the narrow resonances is about 100 kHz, i.e., it is 200 times less than the Doppler width of the rotational–vibrational lines in the ν_3 band of the OsO_4 molecule. It is quite clear that the resonances at the lines of the $Os^{189}O_4$ molecule have a doublet structure, which is in contrast

to $Os^{192}O_4$. This is due to the quadrupole splitting of the rotational–vibrational lines caused by the quadrupole moment of the Os^{189}. The quadrupole structure is usually masked by the Doppler broadening and it cannot be observed by the linear spectroscopy methods. The results reproduced in Fig. 8 demonstrate the effectiveness of the saturation spectroscopy methods free of the Doppler broadening. The structure of spectral lines masked by the Doppler broadening can be studied particularly readily with lasers that emit narrow and tunable lines. The first experiments of this kind were carried out using a cw spin-flip laser. Narrow resonances 200 kHz wide were observed for the lines in the absorption band of H_2O in the region of 1890 cm^{-1}, i.e., the resolution achieved was $R = 3 \times 10^8$.[93]

B. Two-photon spectroscopy

This branch of nonlinear laser spectroscopy free of the Doppler broadening is based on narrow two-photon absorption resonances predicted by Chebotaev et al.[78] Let us consider a two-photon transition of an atom or a molecule in the field of a standing wave of frequency ω (Fig. 9). In the case of particles moving at a velocity $\mathbf{v}$, the traveling waves have the frequency $\omega + \mathbf{k} \cdot \mathbf{v}$. If a particle absorbs both photons from the same traveling wave, only the particles with a specific projection of the

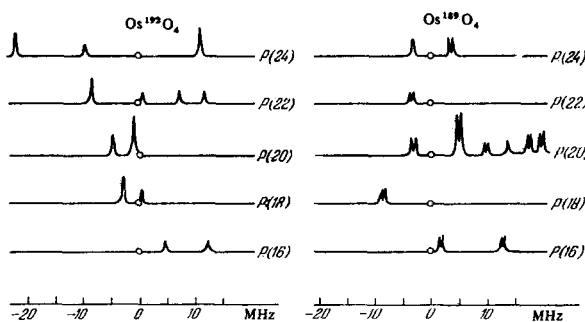FIG. 8. Absorption saturation spectra of the $Os^{192}O_4$ and $Os^{189}O_4$ molecules measured using several lines in the P branch of a CO_2 laser emitting at 10.6 μ. The circles represent the centers of the gain lines of the CO_2 laser.[92]
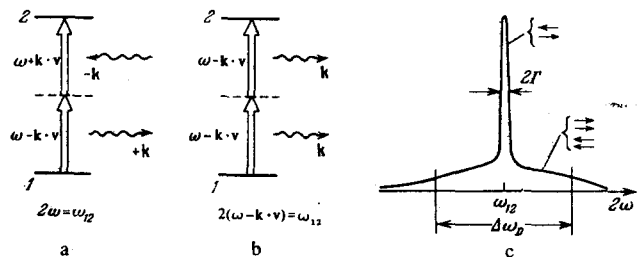

FIG. 9. Explanation of the principle of the two-photon spectroscopy free of the Doppler broadening: the Doppler shift is compensated by the simultaneous absorption of two photons from two waves traveling in opposite directions (a), absence of the Doppler shift from the absorption of unidirectional photons (b), and profile of a narrow two-photon resonance absorption line (c).
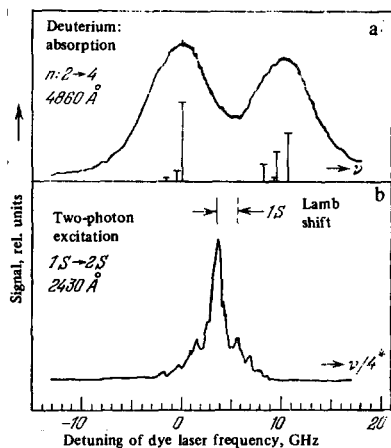
FIG. 10. Profile of the β absorption line in the Balmer series of deuterium with a theoretical fine structure (a) and the simultaneously recorded profile of the two-photon resonance excitation of the 1S-2S transition of deuterium (b).[100]

velocity, satisfying the two-photon resonance condition $\omega_{12} = 2(\omega + \mathbf{k} \cdot \mathbf{v})$, can participate in the absorption process. However, two photons from opposite traveling waves can be absorbed simultaneously. In this case, the two-photon resonance condition requires simply that the doubled value of the field frequency be exactly equal to the two-photon transition frequency of the particle ($\omega_{12} = 2\omega$), i.e., it should coincide exactly with the center of the Doppler-broadened line. In this resonance, all the particles participate in the two-photon absorption, irrespective of their velocity $\mathbf{d}$, and this increases strongly the two-photon absorption signal. The profile of a two-photon absorption line due to a Doppler-broadened transition in the field of a standing wave is shown in Fig. 9c. This profile is the sum of a wide Doppler profile due to the two-photon absorption from two waves traveling in the same direction and of a narrow resonance due to the two-photon absorption of all the particles at the frequency $2\omega = \omega_0$. The amplitude of the resonance peak at the line center should have the enormous contrast $\Delta\omega_D/2\Gamma$, equal to the ratio of the Doppler and homogeneous widths.

The first experimental investigations of narrow two-photon resonances involving transitions in the Na atom were reported in 1974 simultaneously in several papers[94-96]; more recently, the method was applied successfully to the infrared spectroscopy of the CH_3F molecule free of the Doppler broadening.[97]

Chebotaev immediately pointed out[98] the possibility and desirability of obtaining narrow resonances of the two-photon absorption due to the 1S-2S transition in the hydrogen atom. The long lifetime of the 2S state (1/7 sec) made it possible to achieve extremely narrow resonances employing reasonable intensities of the 2430 Å laser radiation.[99] The first successful experiment was carried out recently by Hänsch et al.[100] at Stanford University. The hydrogen atoms were excited directly to the metastable 2S state (in contrast to the one-photon saturation spectroscopy, it was possible to excite directly the forbidden transitions) by 2430 Å laser radi-

ation generated by a pulse dye laser whose frequency was doubled in a nonlinear crystal. The excitation of atoms was deduced from the collision-induced fluorescence line L_α at 1215 Å due to the 2P-1S transition. When photons were absorbed from two opposite waves, resonances of a width less than 2% of the Doppler width were observed. The dye laser radiation before frequency doubling (4860 Å) coincided with the β visible line in the Balmer series, which made it possible to record simultaneously the absorption profile of this line and to make an exact comparison of the energy intervals 1S-2S and (2S, P)-(4S, P, D). The profiles of the two-photon absorption line L_α and of the β absorption line in the Balmer series of deuterium are shown in Fig. 10. Measurements of this kind were used to determine the Lamb shift of the ground state of deuterium (8.3 ± 0.3 GHz) and of hydrogen (8.6 ± 0.8 GHz); this shift had not been measured before for hydrogen.

C. Particle "trapping" method

The Doppler shift of an absorption or emission line can be suppressed by converting the translational motion of a particle to a motion with a limited amplitude smaller than the emission wavelength λ; this can be done, for example, if particles are made to oscillate with an amplitude $a \ll \lambda$. A somewhat similar procedure is adopted in the Dicke buffer gas method in the radio-frequency range[51] when the mean free path of a particle becomes much less than λ. In the optical range, this method requires that the motion of a particle be limited to a very small volume λ^3. The present author[79] suggests using a strong nonresonant standing light wave which can act as a spatially periodic potential field that can "trap" particles with sufficiently low velocities. A neutral particle (an atom or a molecule) subjected to a high-frequency electromagnetic field experiences a force proportional to the gradient of the average square of the electric field intensity. This force pulls in particles into antinodes of the standing wave or expels them from these antinodes.

The depth of potential wells at the antinodes of a standing wave is $U_m = 2\pi\alpha I/c$, where α is the polarizability of a particle in the nonresonant field, I is the radiation intensity, and c is the velocity of light. For a typical atomic or molecular polarizability of $\alpha = 3 \times 10^{-24}$ cm^3, the depth of a potential well in a standing wave of $I = 10^9$ W/cm^2 intensity is $U_m = 3.9 \times 10^{-12}$ eV. Such a potential field can trap only the particles whose kinetic energy is $(1/2)Mv^2 \ll U_m$, i.e., the particles whose velocity is 10^4–10^5 times less than the average thermal velocity v_0. In three-dimensional trapping, one can use a three-dimensional standing wave formed by the intersection between three mutually perpendicular standing waves.[117] In the region of intersection of these waves, particles of velocities less than a certain critical value $v_{cr} = \sqrt{U_m^2/M}$ should be confined to finite motion in an elementary volume $(\lambda/2)^3$. If $\Gamma \ll kv_{cr}$, the Doppler broadening of the spectral lines of such particles should vanish and, at the center of each spectral line, a narrow component with a natural width 2Γ should be observed at the center of each spectral line.

In spite of the obvious difficulties in the practical

realization of this particle trapping method, it deserves attention because of its universal nonresonant nature. A strong optical field of just one frequency outside the resonance transitions of a particle should make it possible to obtain narrow resonances at the centers of Doppler-broadened transitions of any particle.

The idea of particle trapping for the suppression of the Doppler effect is quite practical. This is demonstrated in recent papers,[101,102] in which it is suggested that the spectral line of an ion be narrowed by trapping of ions in a high-frequency field in a region 10 μ in size. A resolution $R > 10^{14}$ is expected for forbidden transitions in the Tl^+, Al^+, and other ions. In this case, the physics of the suppression of the Doppler broadening is the same as in the above trapping of neutral particles in a standing light wave but the actual trapping mechanism is completely different.

D. Comparison of resolving powers

In the absorption saturation spectroscopy, the greatest contribution to the "instrumental" width is made in practice by the resonance broadening effects due to the finite time of the interaction of a particle with the field, known as the transit broadening $\Delta\omega_{tr} \approx v_0/a$ (a is the diameter of the light beam and v_0 is the average thermal velocity of the particles) and by the geometric broadening due to the curvature of the wave front of the beam $(\Delta\omega_g \approx \Delta\omega_{tr}\delta l/\lambda$, where δl is the maximum deviation of the wave front surface from a plane). Hall and Bordé[103] found that a light beam of $a = 30$ cm in diameter with a wave front planar to within a fraction of one wavelength λ was needed for obtaining narrow (less than 2 kHz) absorption saturation resonances for the vibrational–rotational transition $F_1^{(2)}P(7)$ ($\lambda = 3.39$ μ) in CH_4 or for a resolution $R = 5 \times 10^{10}$, necessary for the observation of the splitting of the spectral line due to the recoil effect. A possible way of reducing the transit broadening was suggested in[104]: this method was based on the preferential saturation of particles with very low velocities ($v \ll v_0$), for which the transit broadening in a light beam was small. Recently, Chebotaev et al.[105] were able for the first time to detect this interesting effect experimentally and to resolve the magnetic structure of this CH_4 line with components separated by about 10 kHz; they used a light beam of less than 1 cm in diameter. In the experiments reported in[106,107], it was necessary to use a 5-cm diameter light beam.

The two-photon resonance width is independent of the curvature of the standing wave front because two photons with wave vectors k and $-k$ are absorbed simultaneously at the same point in space. This is the basic difference which distinguishes the two-photon method from the absorption saturation spectroscopy in which narrow resonances are obtained if the wave vector k has exactly the same direction throughout a transverse section through a standing wave. This difference makes it possible to use wider light beams (amounting to tens of centimeters) in the two-photon spectroscopy with a resolution exceeding 10^{10}. Moreover, the contribution of the transit broadening in the two-photon resonances can be made extremely small. In fact, the probability

TABLE 3. Instrumental limitations of resolution in nonlinear laser spectroscopy.

Effect	Absorption saturation spectroscopy	Two-photon spectroscopy	"Trapped" particle spectroscopy
Transit broadening	Yes	Much reduced	No
Geometric broadening	Yes	No	No
Quadratic Doppler effect	Yes	Yes	Very weak
Laser line width	Yes	Yes	Yes
Instrumental resolution limit	$10^{10} - 10^{11}$	$10^{12} - 10^{13}$	$10^{13} - 10^{15}$

of a two-photon transition is independent of the orientation of the velocity of an atom relative to a standing wave. Therefore, using a beam of atoms traveling along a light wave, we can have an interaction length of 100 cm or longer, which corresponds to a transit broadening of just 100 Hz.[99] The principal restriction on the resolution of this method is related to the quadratic Doppler effect which makes the central frequency of a particle dependent on its absolute velocity v. The thermal distribution of the absolute velocities of particles unavoidably broadens a resonance to $\Delta\nu_{qD} \approx \nu_0(kT/Mc^2) \approx \nu_0(v_0/c)^2$ (T is the temperature of the gas, M is the mass of a particle, and c is the velocity of light) and it restricts the resolution of the method to $R \approx (c/v_0)^2 \approx 10^{12}$. Clearly, in all these methods, it is essential to ensure that the line width of the laser radiation used to detect a narrow resonance within the Doppler line is less than the width of this resonance. This means that the laser employed should have a very high short-term frequency stability because it is this stability that is responsible for the broadening of the laser radiation spectrum.

In the method of trapping of slow particles, we can suppress all the effects which limit the resolution of the saturation and two-photon spectroscopy methods with the exception of the last effect, which is the broadening of the laser line used to detect a narrow resonance. A comparison of the instrumental restrictions on the resolution of all three nonlinear laser spectroscopy methods is made in Table III.

E. Comparison of sensitivities

In general, the sensitivity of detection of a narrow resonance by any method is governed by the maximum power ΔP which particles can absorb from a light wave due to a 1–2 transition. The particles responsible for a narrow nonlinear resonance with a homogeneous half-width Γ cannot undergo quantum transitions, stimulated by an optical field, between the levels 1 and 2 at a rate exceeding Γ. Consequently, the maximum power absorbed per unit volume is

$$\Delta P \lesssim \hbar\omega_{12}\Gamma N_{in}, \tag{4.1}$$

where N_{in} is the density of the particles interacting

resonantly with the light wave. In the absorption saturation spectroscopy, only a small proportion of the particles is in resonance with the field and these particles have a definite projection of the velocity, i.e., $N_{1n} \approx (\Gamma/ku)N_0$, where N_0 is the total density of the particles at the levels 1 and 2. Thus, the sensitivity of this method decreases proportionally to the reduction in the width of the narrow resonance.

In the two-photon spectroscopy, all the particles are in resonance with the standing light wave irrespective of their velocity. Therefore, in this method, $N_{1n} = N_0$, which results in a considerable gain in the sensitivity method by a factor of the order of $ku/\Gamma \approx 10^3 - 10^5$ when very narrow resonances are observed.

In the particle-trapping spectroscopy, the number of interacting particles N_{1n} is essentially equal to the number of trapped particles N_t. In the case of complete (three-dimensional) trapping of particles in the region of intersection between three mutually perpendicular standing light waves, i.e., when particles are trapped in volumes of the order of $(\lambda/2)^3$, the sensitivity decreases proportionally to $(v_{cr}/v)^3$. The exceptionally small proportion of particles in an equilibrium gas with an absolute velocity $v < v_{cr}$ requires the accumulation of slow particles for recording resonances.

The sensitivity of any of the nonlinear spectroscopy methods depends strongly on the technique used to measure the power ΔP absorbed in a gas. It is usual to measure the change in the power density P of a wave used to detect a narrow resonance after this wave has passed through a gas-filled cell. If the absorption is weak $(\Delta P \ll P)$, such a change is negligible and the sensitivity is limited by the shot noise of the detector which is due to the main wave of power density P reaching the detector. It is much more convenient to record directly the absorbed power density ΔP. This can be done, for example, if the excited particles fluoresce. A narrow resonance can then be recorded using the change in the fluorescence intensity. [90, 91] In this case, the main wave does not reach the detector and the sensitivity in recording narrow resonances is much greater. For example, narrow resonances of the fluorescence of the CO_2 molecules emitted as a result of absorption saturation of the CO_2 laser radiation were recorded in[108] at very low pressures of CO_2 (down to 10^{-5} Torr). The same method for detection of narrow resonances is fully applicable also in the two-photon and trapped-particle spectroscopy. For example, when trapped particles are detected by the fluorescence method using a tunable visible or ultraviolet laser, it is possible—at least in principle—to reach a sensitivity sufficient to record a single particle. In particular, this possibility is considered in[102] for a Tl^+ ion trapped in an electromagnetic field.

The nonlinear laser spectroscopy methods are developing rapidly and we can now distinguish three main types of application: obtaining new spectroscopic information, precision measurements of the constants and the associated metrological applications, and applied spectroscopy.

F. New spectroscopic information

Experiments with a resolution of 10^8 are now quite frequent. In the best experiments carried out by the absorption saturation method, a resolution of 10^{10} has been achieved, which is approximately 10^5 times greater than the resolution of the best classical spectrometers and 10^4 times greater than the resolution of linear laser spectrometers. A comparison of the nonlinear laser spectroscopy methods shows that one can expect a resolution of the order of $10^{13} - 10^{15}$, which is restricted by the fundamental limit representing the natural width of a laser line. Therefore, it is in order to ask the following question: what new spectroscopic information will become available as a result of the application of the nonlinear laser spectroscopy methods free of the Doppler broadening to atoms and molecules.

The following spectroscopic effects in atoms should be measured free of the Doppler broadening:

1) the fine structure of higher states $(R = 10^5 - 10^7)$;

2) the isotopic structure $(10^5 - 10^7)$;

3) the hyperfine structure, including that of atoms with isomeric nuclei $(10^5 - 10^8)$;

4) the relativistic effects, particularly the Lamb shift $(10^6 - 10^8)$;

5) the radiative broadening of spectral lines $(10^6 - 10^9)$;

6) the collisional broadening of spectral lines $(10^7 - 10^9$ at a pressure of 1 Torr); the values in parentheses give the resolution necessary for these measurements.

The multiplet or fine structure is usually resolved satisfactorily by the classical methods but, in the case of higher states, the fine splitting decreases proportionally to n^3 (n is the principal quantum number) and it is lost because of the Doppler width. An investigation of the isotopic and hyperfine structures due to the spin and quadrupole moments of the nuclei, including excited nuclei (isomeric hyperfine structure), requires a resolution in the range $10^5 - 10^8$. Many of the isotopic and hyperfine components can be resolved by classical instruments with a high resolving power (Fabry–Perot interferometer) but a full study of the structure requires penetration into the Doppler width. Before the development of the nonlinear laser spectroscopy, this was sometimes achieved by narrowing the spectral lines in an atomic beam or by radiofrequency spectroscopy of the ground and some excited states. The hyperfine structure of the D lines of Na can be detected using an atomic beam, whereas the absorption saturation spectroscopy makes it possible to determine the same structure in a low-pressure gas.[109] A classical example is the Lamb shift, which, in the case of, say, the $2S$ level of the hydrogen atom, is an order of magnitude smaller than the Doppler width of the H_α line. In the past, the detection of this shift required the use of the radiofrequency spectroscopy of excited states of atoms in a beam.[110] Nowadays, such measurements can be made by the saturation absorption spectroscopy[111] and by the two-photon spectroscopy[100] methods.

The classical molecular spectroscopy methods, particularly those in the infrared range, do not ensure an acceptable resolution. Therefore, infrared spectroscopy of molecules with a resolution better than 10^5 can be performed only with the aid of lasers. The following spectroscopic effects in the molecular infrared transitions require the suppression of the Doppler broadening:

1) the collisional broadening of spectral lines ($R = 10^7 - 10^8$ at a pressure of 1 Torr);

2) the Stark and Zeeman effects in weak fields ($10^6 - 10^9$);

3) the hyperfine structure due to the quadrupole interaction ($10^6 - 10^8$);

4) the hyperfine magnetic structure ($10^9 - 10^{11}$);

5) the isomeric shift due to the excitation of nuclei ($10^8 - 10^{10}$);

6) the difference between the frequencies of left-handed and right-handed molecules due to weak interactions ($10^{13} - 10^{15}$).

Above all, the spectroscopy free of the Doppler broadening allows us to study collisions at low gas pressures when the collisional broadening is much less than the Doppler effect. At very low gas pressures, the collision frequency becomes comparable with the level decay rate and, therefore, the profiles of narrow resonances begin to be affected by the elastic scattering of the colliding particles. This gives rise to, for example, nonlinear pressure dependences of the broadening and frequency shift of narrow resonances of vibrational-rotational transitions.[112,113] The nonlinear nature of the pressure dependences of the broadening and shift is manifested in that range of pressures in which the Doppler frequency shift due to the elastic scattering of molecules through small angles becomes comparable with the homogeneous (collisional) width of a narrow resonance. Some modification of the absorption saturation method, involving observation of a narrow resonance at a frequency shifted relative to the center of a Doppler line, provides a simple means for the determination of the dependence of the collisional broadening cross section on the velocity of the colliding particles.[114] Naturally, all these experiments can be carried out in external electric and magnetic fields so as to obtain information on the Stark and Zeeman effects in molecular transitions[115-117] and, in particular, fairly precise measurements can be made of the dipole moments of excited molecular states.[116]

A completely new possibility is the measurement of the hyperfine structure of vibrational-rotational transitions due to the quadrupole and magnetic interactions. The quadrupole interaction causes splitting of the vibrational-rotational lines by an amount corresponding to $10^6 - 10^7$ Hz, which depends on the quadrupole interaction constant and the angular momentum of a molecule. An example of an experimental observation of the quadrupole structure of the $Os^{189}O_4$ molecule is shown in Fig. 8. The magnetic interaction between the angular momentum of a molecule and the nuclear spin causes a

much weaker splitting by an amount lying in the range $10^3 - 10^5$ Hz. This splitting can be detected only if the resolution is $10^9 - 10^{11}$. The first successful detection of the magnetic hyperfine structure in a vibrational-rotational spectrum was carried out by Hall and Bordé[106] on the $C^{12}H_4$ molecules.

The excitation of a nucleus in a molecule should alter the vibrational frequencies because the excitation energy of the nucleus ΔE_n is equivalent to an increase in the nuclear mass by an amount $\Delta m = \Delta E_n / c^2$ (isomeric shift).[118] A possible candidate for the detection of the isomeric shift in the vibrational spectra is the OsO_4 molecule with an isomeric (long-lived) excited Os nucleus. The shift of the vibration frequency ν_3 of the OsO_4 molecule due to an increase in the internal energy of the Os nucleus should lie between 0.3 and 2.0 MHz when the nuclear energy is between 30 and 170 keV, depending on the nuclear isomer of osmium.[92] This effect opens up the possibility of measuring, in principle, the energy of metastable nuclei with a high precision irrespective of the nature of radioactive decay by the application of infrared molecular spectroscopy methods.

There is one further extremely fine effect in the molecular spectra which lies outside the range of the present experimental methods but may become detectable by nonlinear laser spectroscopy methods in future. The effect is due to the difference between the energies of levels of two molecules which are mirror images of one another because of parity nonconservation in weak interactions of electrons and nucleons in a molecule.[119] The physical origin is the presence of a small admixture of an odd potential of the interaction between electrons and nucleons forming a molecule. This odd interaction lifts the degeneracy of the energy levels of levo and dextro molecules so that, for example, the vibrational energies become different by an extremely small amount, of the order of $\Delta E \approx 10^{-15} E_{vib}$. Figure 11 shows an example of two simplest mirror-symmetric molecules (methane with different halogens instead of hydrogen), which should exhibit this frequency splitting.[1]

G. Precision spectroscopy

The use of narrow nonlinear resonances provides two ways of increasing considerably the precision of measurement of the spectral line positions.

Firstly, narrow saturation resonances have already been used to establish a new length standard ($He-Ne/I_2$ laser emitting at 6328 Å)[120-122] with a reproducibility better than 10^{-10} (stabilization of the laser emission frequency with the aid of narrow molecular resonances is reviewed in[123]), which can be used to carry out interferometric comparisons of the laser transition wavelengths with a precision of at least 10^{-10}.[121] This, in

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[1]The detection of this effect might explain an observation relating to biological isomerism: all the proteins occurring in nature are constructed from L-amino acids (left-handed isomeric forms). This biological isomerism was discovered by Pasteur over a hundred years ago but has not yet been explained satisfactorily.
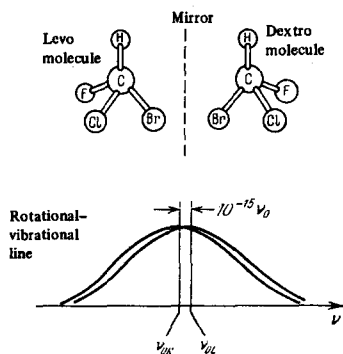
FIG. 11. Possible splitting of the frequency of a rotational-vibrational transition of two stereoisomeric forms of the simplest CHFClBr molecule due to parity nonconservation in weak interactions of elementary particles in a molecule.

combination with the saturation spectroscopy methods for the exact determination of the centers of the H_α and D_α spectral lines, made it possible to carry out precision measurements of the Rydberg constant.[124] The new value of the Rydberg constant R_∞ = 109 737. 3143(10) cm^{-1} is subject to an error an order of magnitude smaller than the previous value.

Secondly, instead of measuring the wavelength of a transition, it is now possible to determine the frequency. Until recently, the transition frequencies were determined spectroscopically only indirectly and with a relatively low precision. The measured quantity has been the wavelength of a transition and the known value of the velocity of light has been used to calculate the frequency. The error in such calculations has always been greater than 10^{-7} because of the error in the velocity of light. The saturation laser spectroscopy and the methods developed for the direct measurement of the frequency of optical oscillations have made it possible to increase the precision of the determination of the velocity of light by a factor of about 10^2. The new velocity of light is c = 299 792 456. 2(1. 2) m/sec.[122,125] This value, in combination with the high precision of the interference methods for the comparison of laser wavelengths with the wavelength of the He-Ne/I_2 laser, has made it possible to determine the transition frequencies and wavelengths with an error not exceeding 10^{-9}. The recently developed methods for measuring the absolute frequency of optical oscillations[126,127] have made made it possible to determine directly the frequencies of transitions with the same precision as in the measurement of the frequency of optical oscillations with the aid of the international time standard. This basically new technique is still in its early stages but it is exceptionally promising in combination with simple and efficient methods for nonlinear conversion of optical frequencies.

H. Applied spectroscopy

A nonlinear laser spectrometer for measurements on atoms and molecules free of the Doppler broadening and with a resolution $R \gg \nu_0/\Delta\nu_D$, where $\Delta\nu_D$ is the Doppler width of spectral lines in a gas, has at least two important advantages in applied spectroscopy. Firstly, the

information capacity of a spectral interval $\Delta\nu$ of such a spectrometer is

$$P = P_0 R \frac{\Delta\nu}{\nu_0} \text{ (bits)}, \qquad (4.2)$$

where P_0 is the number of information units obtained in a resolvable spectral interval ν_0/R by measuring the intensity of the spectrum at a given frequency. For example, for a resolution $R = 10^8$, which is standard in nonlinear spectroscopy, and for a spectral interval $\Delta\nu$ = 1 cm^{-1}, the information capacity at $\nu_0 = 3 \times 10^3$ cm^{-1} is $P_0 \times 3 \times 10^4$ bits, i. e., if $P_0 = 10$, we have $P = 3 \times 10^5$ bits. The information capacity of a very good classical infrared spectrometer with a resolution of 0. 1 cm^{-1} is about 10^2 bits in the same spectral interval. Secondly, the overlap of a large number of rotational-vibrational lines, separated by intervals smaller than the Doppler width, is typical of complex molecules. In this case, a spectroscopic analysis can be carried out only over vibrational bands when the maximum number of information units in one octave in the infrared region is

$$P_{max} \approx P_0 \frac{\nu_0}{\delta\nu_{vib}}, \qquad (4.3)$$

where $\delta\nu_{vib}$ is the vibrational band width. This is a fairly serious limitation of the capabilities of infrared molecular spectroscopy. This does not apply to the nonlinear spectroscopy so that information on complex molecular mixtures sufficient for quantitative and qualitative spectroscopic analysis can be obtained from a relatively narrow spectral interval even inside overlapping absorption bands of molecules in a mixture. The first successful experiments involving the use of a nonlinear spectrometer for this purpose were reported in[128], where a spectroscopic investigation was made of the C-H bonds in various hydrocarbons near 3. 4 μ.

5. RAMAN LASER SPECTROSCOPY

The Raman scattering method is a powerful tool for investigating the molecular structure which has been growing in importance even before the appearance of the laser but has been limited mainly to scientific investigations because of the very low intensity of the scattered light. Infrared absorption spectra have been used almost exclusively in practical spectroscopic analysis before the advent of the laser. The construction of various practical lasers operating at fixed frequencies in the visible range has altered the situation drastically. The properties of laser radiation—its directionality, monochromaticity, high intensity, and absence of a continuous background—make the laser a practically ideal source for Raman spectroscopy. The Raman method is now used widely in various investigations in solid-state physics (scattering by photons, spin waves, and electrons) and chemistry (investigations of molecular complexes and unstable molecules). The main results on the laser Raman spectroscopy can be found in books[129-131] and reviews (see[132] for the scattering in solids and[133] for the scattering in gases). Here, we shall consider briefly only those aspects of the Raman laser spectroscopy which are based essentially on the use of the laser and are practically unrealizable if a classical source of light is used.
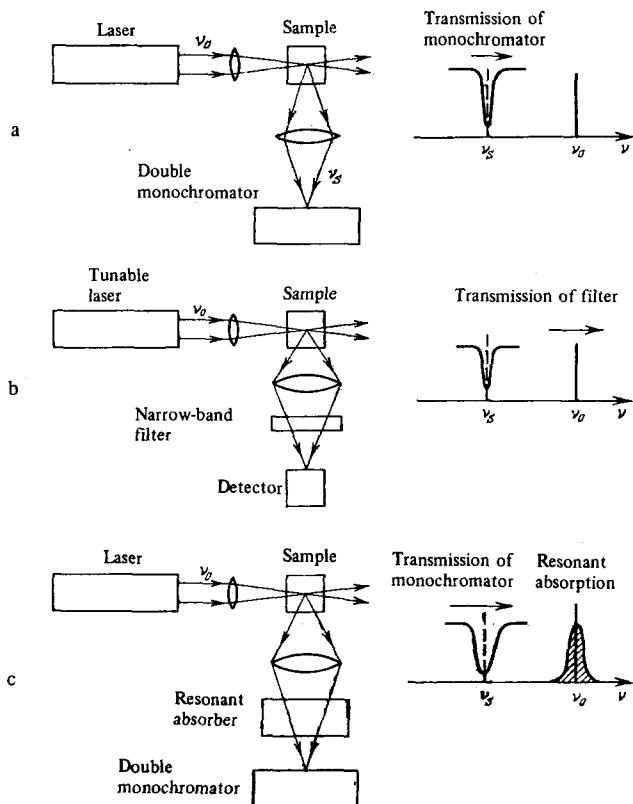
FIG. 12. Various configurations used in laser Raman spectrometers: a) general configuration with a laser and a double monochromator; b) configuration with a narrow-band filter and scanned exciting radiation frequency; c) configuration with a cell absorbing resonantly at the laser frequency.

A. Spontaneous Raman spectroscopy

The intensities of the Raman lines are very low. Therefore, the presence of even a weak scattered-light background in the vicinity of the excitation line beyond the monochromator makes it impossible to detect Raman lines. The scattered-light background is usually reduced by the employment of double and triple high-resolution monochromators. An important parameter of their quality is the background of scattered light for a given detuning from the excitation frequency. A high-resolution monochromator (Fig. 12a) can be replaced by a narrow-band filter with a fixed pass band and the Raman spectrum can be scanned by varying the laser emission frequency (Fig. 12b). A tunable laser with a narrow spectrum and a low spontaneous radiation background can be constructed more easily than a monochromator with similar spectral characteristics. The sensitivity of the laser system was demonstrated in[134], where a set of narrow-band interference filters was used in conjunction with a tunable dye laser. A different method is based on the suppression of the scattered background at the excitation frequency, i.e., on the suppression of the elastically scattered light in the sample itself and of the scattered-light background in the monochromator, by a resonant absorber placed directly in front of a detector whose frequency is exactly equal to the laser frequency (Fig. 12c). A successful example of this system is an argon laser emitting at

$\lambda = 5145$ Å and an I_2 absorption cell.

The use of a laser makes it possible to reach the ultimate resolution governed by the width of the Raman lines. In the case of gases, laser excitation makes it possible, in principle, to reduce very considerably the limitation imposed on the Raman spectral resolution by the Doppler broadening.[135] This is possible if use is made of monochromatic and directional laser radiation. In fact, the frequency shift of the Raman scattering ω_S relative to the laser frequency ω_L depends on the velocity of the scattering particle $\mathbf{v}$:

$$\omega_L - \omega_S = \omega_{12} + (\mathbf{k}_L - \mathbf{k}_S)\,\mathbf{v}, \qquad (5.1)$$

where $\mathbf{k}_L$ and $\mathbf{k}_S$ are the wave vectors of the laser and scattered radiation, respectively; ω_{12} is the molecular vibration frequency. Therefore, the width of a line due to the Raman scattering in the forward direction is governed by the homogeneous (collisional) width of the scattering line 2Γ and by a small compensated part of the Doppler width:

$$\Delta\omega_{sc}^+ = 2\Gamma + \frac{\omega_{12}}{\omega_L}\Delta\omega_D. \qquad (5.2)$$

The width of the backward-scattered line includes the double Doppler broadening:

$$\Delta\omega_{sc}^- = 2\Gamma + \left(1 + \frac{\omega_S}{\omega_L}\right)\Delta\omega_D. \qquad (5.3)$$

This reduction in the Doppler width is of the same origin as the suppression of the Doppler broadening in the two-photon transitions considered in Sec. 4. If a two-photon transition, shown in Fig. 9a, is due to photons of unequal frequencies ω_1 and ω_2, the residual Doppler shift is $(\mathbf{k}_1 + \mathbf{k}_2)\cdot\mathbf{v}$. The Doppler shift can be minimized if photons move opposite to one another. In the Raman scattering case, a virtual intermediate level is located outside the initial and final states, i.e., the transition energy is equal to the difference between and not to the sum of the photon energies. Therefore, the residual Doppler shift is $(\mathbf{k}_1 - \mathbf{k}_2)\cdot\mathbf{v}$. This effect was ignored in[135] and led to an incorrect conclusion in the review[133] that the line width could be reduced right down to 0.001 cm^{-1} by a suitable reduction of the pressure. In fact, in the experiments on H_2 reported in[135], the collisional broadening at 2 atm was 2.5 times smaller than the residual Doppler broadening and a further reduction in pressure would not be helpful.

The resolution in the forward scattering is increased if the scattered radiation is recorded in a narrow solid angle. It seems to the present author that this method can be improved considerably by determining the gain line profile at the Raman scattering frequency with an additional probe beam produced by a tunable laser and collinear with the exciting beam. The difficulty in recording gain lines at the $10^{-5}-10^{-7}$ cm^{-1} level can be fully overcome by applying the optoacoustic method to the detection of the energy absorbed in the Raman scattering. In such experiments, measurements should be made of the optoacoustic signal in a molecular gas when the difference between the frequencies of two lasers is tuned to the frequency of molecular vibrations.

B. Inverse Raman spectroscopy

If a molecular medium is illuminated simultaneously by intense monochromatic radiation at a frequency ω_0 and by radiation with a continuous spectrum of higher frequencies, we can observe stimulated Raman scattering in which the strong field of frequency ω_0 stimulates the participation in the scattering process of photons of frequency $\omega_0 + \Omega$ from the continuous spectrum, where Ω is the frequency of molecular vibrations. In contrast to the conventional Raman scattering, the strong field acts at the Stokes frequency relative to the weak field at the frequency $\omega_0 + \Omega$. This results in the absorption of the frequencies $\omega_0 + \Omega$ from the continuum and it is usually called the inverse Raman scattering. The effect was first observed experimentally in[136].

A useful feature of the inverse Raman scattering is that it can be used to record all the spontaneous scattering lines of molecules in a short time. A shortcoming of this method is the relatively low sensitivity in the detection of molecules in mixtures. The sensitivity can be increased by using a more sensitive method for the detection of weak absorption lines in a continuous spectrum. The intraresonator absorption method, considered in Chap. 3, is very effective in this application. The first increase in the sensitivity of the inverse Raman scattering by this method was reported in[137]. A scattering medium was placed inside a dye laser resonator and the continuum was provided by the wide-band radiation emitted by the same laser. The scattering medium was illuminated simultaneously by a high-power monochromatic pulse of frequency ω_0, which induced inverse Raman scattering at frequencies $\omega_0 + \Omega$ lying within a wide emission line of the dye. In this way, the detection sensitivity was increased by a factor of 10^2 compared with the case when the scattering medium was outside the resonator. As shown in Sec. 3, the sensitivity gain could be increased considerably by using longer stimulated emission times but this would be at the expense of a corresponding reduction in the temporal resolution.

C. Active Raman spectroscopy

Stimulated Raman scattering in the field of high-power laser radiation has been investigated since 1962 but the use of the Raman method in spectroscopy is very restricted by such nonlinear effects as the strong competition between the Raman lines, influence of other nonlinear processes (spontaneous mode locking and self-modulation), and the existence of an excitation intensity threshold. All these effects are due to the fact that the stimulated Raman scattering is essentially a development of an instability in the medium in which photons are created at Raman frequencies in a random manner. Currently, a new—active—Raman spectroscopy is being developed intensively and this method occupies an intermediate position between the spontaneous and stimulated Raman scattering. This new method combines the extensive spectroscopic capabilities of the spontaneous scattering method and the most important feature of the stimulated Raman scattering, which is the high intensity of the scattering lines. We can say that the active Raman spectroscopy method is
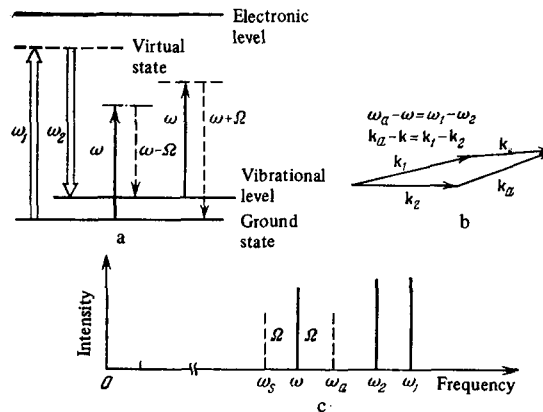

FIG. 13. Active coherent Raman scattering of a probing wave (ω, k) by coherent molecular vibrations of frequency Ω, excited by two coherent waves (ω_1, k_1) and (ω_2, k_2): a) energy level scheme; b) condition for frequency and spatial phase matching at the anti-Stokes frequency; c) field frequencies.

based on a controlled generation of photons at Raman frequencies.

The active Raman spectroscopy method is based on the buildup of molecular vibrations active in the Raman effect when molecules are subjected to the field of sufficiently strong laser beams of frequencies ω_1 and ω_2 which differ by an amount exactly equal to the molecular vibration frequency Ω. Two spatially coherent waves $\mathscr{E}_1 \exp[i(\omega_1 t - k_1 \cdot r)]$ and $\mathscr{E}_2 \exp[i(\omega_2 t - k_2 \cdot r)]$ excite phonon vibrations coherently throughout the interaction zone, i.e., the amplitude of the phonon wave in the medium is of the form $\mathscr{E}_1 \mathscr{E}_2 \exp[i(k_1 - k_2) \cdot r]$. If a probing field of frequency ω is now directed to the interaction zone, scattering takes place on the phonon vibrations and, consequently, spectral lines appear at the frequencies $\omega_a = \omega + \Omega$ and $\omega_s = \omega - \Omega$ (Fig. 13), and the intensities of these lines are much higher than the intensity of the corresponding stimulated Raman scattering. However, the intensities of the strong waves ω_1 and ω_2 and of the probe wave are all below the stimulated Raman scattering threshold and, therefore, no random instabilities or line competition takes place. The difference between the frequencies of the laser waves $\omega_1 - \omega_2$ can be varied and thus all the molecular vibrations of the medium active in the stimulated Raman effect can be excited in turn, i.e., the whole Raman spectrum of the medium can be recorded.

The probing light wave $\mathscr{E} \exp[i(\omega t - k \cdot r)]$ is scattered by the spatial grating of the phase-locked molecular vibrations in the medium. Therefore, as is usual in the interaction of plane waves, there is phase-matching direction along which the scattered-wave amplitude $\mathscr{E}_s \exp[i(\omega_{s,a} t - k_{s,a} \cdot r)]$ has its maximum value:

$$
\begin{aligned}
k_1 - k_2 &= k - k_s, \\
k_1 - k_2 &= k_a - k.
\end{aligned}
\tag{5.4}
$$

In the phase-matched case, the amplitude of the scattered wave is proportional to the path l of this wave in the medium and, consequently, the scattering intensity is proportional to l^2. In the spontaneous Raman scat-

tering, the molecular vibrations are not in phase and the scattering intensity is proportional to l. The intensity of the scattered wave is related to the intensities of the other waves by

$$I_{a,s} \propto I_1 I_2 I,$$ (5.5)

i. e., it is proportional to the intensities of all three waves. In the active Raman spectroscopy, the intensities of the Stokes and anti-Stokes components are the same along the phase-matched direction, whereas, in the spontaneous isotropic Raman spectroscopy, the Stokes component predominates.

We have to distinguish two varieties of the active Raman spectroscopy, which are the coherent and noncoherent methods. The coherent active Raman scattering, sometimes called the coherent anti-Stokes scattering, occurs along the phase-matched directions k_s for the Stokes wave and k_a for the anti-Stokes wave. This scattering is due to the phase-locking of the molecular vibrations throughout the medium. If, for example, the exciting fields ω_1 and ω_2 are suddenly switched off, this directional Raman scattering decays in the time T_2 it takes for the molecular vibrations to become out of phase with one another. Thus, the coherent active Raman scattering is due to the polarization of the medium at the frequency Ω and not due to the populations of the molecular levels. However, sufficiently strong fields ω_1 and ω_2 can populate considerably a vibrational molecular level $\hbar\Omega$ and, consequently, we may observe the usual isotropic Raman scattering at the anti-Stokes frequency due to the vibrationally excited molecules, accompanied by real transitions of molecules from the excited to the ground state. If the strong fields of frequencies ω_1 and ω_2 are switched off suddenly, such noncoherent Raman scattering at the frequency ω_a decays in the relaxation time T_1 of the vibrational level population. The noncoherent isotropic Raman scattering at the frequency ω_s corresponds to the ordinary spontaneous scattering which is independent of the fields ℓ_1 and ℓ_2. Thus, if we record the coherent (directional) and noncoherent (nondirectional) active Raman scattering at the anti-Stokes frequency, we can determine separately the dephasing time (T_2) and the relaxation time (T_1) of the molecular vibrations.

The first experimental studies of the active Raman scattering by coherent molecular vibrations[138] were carried out in the course of a study of the dispersion of the Raman susceptibility of some organic liquids. A detailed analysis of the scattering of light by coherent molecular vibrations was made in[139]. This phenomenon was subsequently investigated using lasers emitted at two fixed frequencies. However, the latent possibilities of the active Raman scattering method were only realized when molecular vibrations were excited with tunable lasers (dye lasers[140,141] and parametric oscillators[142]). A detailed discussion of the active Raman spectroscopy was recently published by Akhmanov and Koroteev.[143]

Figure 14 shows typical experimental results obtained by the active coherent Raman spectroscopy (for the H_2 molecule).[144] The difference between the frequencies
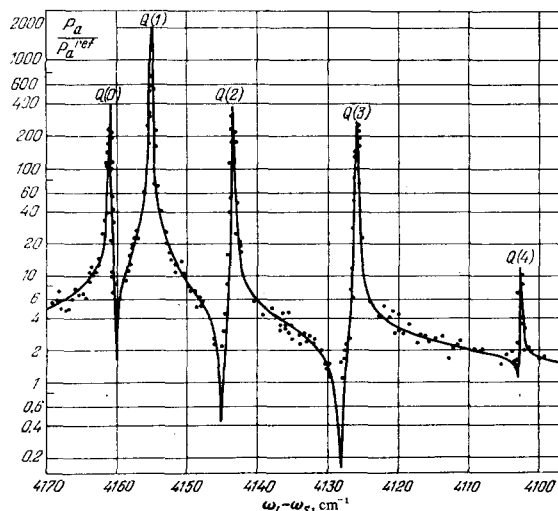

FIG. 14. Intensity of an anti-Stokes wave generated by the scattering of a wave ω_1 by coherent vibrations of the hydrogen molecule (1 atm, 300 °K) excited by light waves of frequencies ω_L and ω_S.[144]

of two lasers was tuned in the vicinity of the frequency of vibrational–rotational transitions in H_2. Coherent Raman scattering at the anti-Stokes frequency $\omega_a = \omega_3$ $= 2\omega_1 - \omega_2$ is observed. A change in the scattering intensity by four orders of magnitude was found in the resonance region. The profile of the active coherent Raman line was proportional to the third-order nonlinear susceptibility $|\chi^{(3)}|$.[2]

The active Raman scattering method is characterized by a considerable gain in the sensitivity compared with the spontaneous Raman spectroscopy. The signal depends quadratically on the length of the sample and on the intensity of the exciting waves (for $I_1 = I_2$). Even if the spatial phase-matching condition is not satisfied rigorously, for example, if $l_{coh} \approx 1$ mm, it is quite realistic to expect an increase in the sensitivity by a factor of 10^4–10^5. Another feature of the coherent active Raman spectroscopy method is the feasibility of investigating media emitting fairly strong wide-band fluorescence. Since the scattering signal is observed in the anti-Stokes frequency along a specific direction, it is possible to eliminate practically completely the influence of the wide-band isotropic fluorescence lying in the Stokes region. This advantage should be particularly important in studies of many molecular compounds in biology. The first experiments of this kind resulted in an increase in the Raman signal by a factor of 10^5 above the fluorescence level.[145]

6. TWO-PHOTON ABSORPTION SPECTROSCOPY

Two-photon transitions make it possible to extend considerably the capabilities of not only conventional but also of laser spectroscopy of one-photon transitions. Many aspects of the two-photon spectroscopy have already been considered above. Methods for obtaining narrow two-phonon resonances free of the Doppler broadening by simultaneous absorption of two photons traveling in opposite directions by a particle moving in a gas are considered in Sec. 4. The preceding section

deals with the Raman scattering of light, which is a two-photon process that can be observed in the scattering or absorption (inverse Raman scattering). To avoid misunderstanding with the Raman scattering, we shall define the two-photon absorption as involving a transition between energy levels differing by an amount $E_2 - E_1$ equal to the energy of the sum of the absorbed photons $\hbar\omega_1 + \hbar\omega_2$. Such two-photon absorption was first observed in[146].

Two-photon transitions have the following features which are important in spectroscopy.

Firstly, the two-photon transitions are subject to selection rules different from those that apply to one-photon transitions. For example, in the dipole approximation, a two-photon transition is allowed only between the states of the same parity, whereas one-photon transitions may take place between states of different parity. Moreover, in principle, more information can be obtained from two-photon than from one-photon spectra because, in the former case, the absorption is a function of two frequencies ω_1 and ω_2.

Secondly, two-photon absorption may excite states of a particle which would require, in the one-photon case, a quantum that would be absorbed by the matrix in which the particle is located. Thus, in principle, selective excitation of particles inside an absorbing medium is possible as a result of two-photon absorption.

Two-photon absorption in a condensed medium is independent of the relative orientations of the directions of the light waves ω_1 and ω_2 (this is the essential difference from the same type of absorption in a gas). However, two-photon absorption depends strongly on the polarization of light waves. This dependence differs strongly from the polarization dependence of the one-photon absorption and, in particular, it is observed even in an isotropic medium. This polarization dependence is also of interest in spectroscopy since it can yield information on the symmetry of the quantum states participating in a two-photon transition. More detailed information on these and many other features of the two-photon absorption spectroscopy and on specific results obtained for various substances can be found in the reviews.[147,148]

In contrast to several other laser spectroscopy methods, the two-photon absorption spectroscopy is still at the research stage. Many two-photon spectroscopy methods are not yet fully developed. For example, measurement of the absolute two-photon absorption cross section is a complex process because such measurements are sensitive to the spatial and temporal inhomogeneity of the laser radiation. It should be noted that a method which is convenient for such measurements was recently suggested in[149]. The smallness of the two-photon absorption coefficient makes it difficult to apply this method to particles present in low concentrations ($< 10^{20}$ cm^{-3}). This difficulty can be overcome by applying the intraresonator cell method, described in Sec. 3, to the detection of weak absorption lines. The apparatus used in such experiments, first carried out in[150], is similar to that used in the detection of weak inverse Raman scattering lines described in Sec. 5.

There is no doubt that the development of tunable lasers and methods for detection of weak absorption lines will result in a more extensive use of two-photon absorption in the spectroscopy of condensed media and in utilization of its specific features, particularly the ability to investigate the levels of particles inside the absorption bands of the matrix, which are not accessible to one-photon spectroscopy methods.

7. SELECTIVE DETECTION OF LOW CONCENTRATIONS OF ATOMS AND MOLECULES

One of the most valuable and important applications of the laser spectroscopy methods discussed above is the analysis of traces of atoms and molecules. This application is important in the laboratory, because it increases the sensitivity of the apparatus and, outside the laboratory, in the detection of microscopic amounts of atoms and molecules in the environment (atmosphere, hydrosphere, ionosphere, etc.). This type of application has become particularly important because of the increasing need to monitor pollution of environment by industrial waste products. Other applications include the search for useful minerals on the basis of gases emitted by them to the atmosphere, which can be done with a much higher reproducibility over larger areas than by the existing methods. The laser spectroscopy methods will make it possible, in most cases, to detect traces of atoms and molecules in amounts which would be impossible to detect by any other method. This applies particularly to the remote detection of atoms and molecules when there is no possibility of making a local analysis.

A. Local detection of atoms

The local detection of atoms by laser spectroscopy methods can be made with a sensitivity much higher than that of the classical atomic analytic spectroscopy methods. In particular, the laser excitation of the fluorescence of Na atoms under pulse conditions makes it possible to attain the sensitivity amounting to one photoelectron per pulse from an excited volume containing 10^5 atoms[151] and, under continuous conditions, it is possible to detect resonance radiation scattered by just one atom. If the continuous radiation saturates an absorption transition in an atom, the atom spends only half its time in the excited state and, consequently, the resonantly reemitted power is $A_{21}\hbar\omega/2$, where A_{21} is the Einstein coefficient for spontaneous emission. In the case of the D_2 resonance line of Na, the excited-atom lifetime is 16 nsec and, consequently, an atom of Na scatters 3.2×10^7 photons in 1 sec if the exciting radiation has a power several times higher than the saturation power $I_s = 2.1 \times 10^{-2}$ W/cm^2. Further development of tunable lasers, particularly those emitting in the ultraviolet region where the resonance peaks of the majority of elements are located, should result in the development of extremely sensitive laser-fluorescence detectors of traces of atoms.

Single atoms can also be detected by selective two-

step ionization.[110,152] This method is based on the
selective excitation of an atom to a desired quantum
state and subsequent photoionization of only the excited
atoms by additional laser radiation. The photon energy
of the ionizing radiation $\hbar\omega_2$ is selected on the basis of

$$E_i - \hbar\omega_1 < \hbar\omega_2 < E_i, \qquad (7.1)$$

where E_i is the ionization energy of an atom and $\hbar\omega_1$ is
the energy of the excited level. If the intensity of the
ionizing radiation is $P_2 \gtrsim \hbar\omega_2/2\sigma_i\tau_1$, where σ_i is the ion-
ization cross section and τ_1 is the excited state lifetime,
each excited atom should become ionized. The first
selective two-step ionization experiments were carried
out on Rb atoms[152] and, more recently, it was re-
ported that the selective ionization of these atoms had a
quantum efficiency close to unity.[153] In principle, this
method should make it possible to detect single atoms
but—in contrast to the fluorescence method—it is de-
structive. The ionization method is suitable for the
detection of atoms in metastable states when the fluo-
rescence is very weak and a relatively low power is
needed for the photoionization. Moreover, the photo-
ionization method of selective detection of atoms has a
very important advantage over all the other methods
because it provides means for extracting the detected
atom by external electric and magnetic fields. This
property is basic to laser isotope separation methods
and to preparation of exceptionally pure substances.
The method of selective ionization of atoms is being
extensively investigated as one of the isotope separa-
tion methods (see the review in[154]). These investiga-
tions should provide a new spectroscopic method for
the detection and extraction of atoms of a specified kind
from a mixture.

B. Local detection of molecules

The local detection of molecules is an exceptionally
difficult problem which can be solved to a varying ex-
tent for three types of molecule: 1) the simplest di-
atomic and triatomic molecules and radicals; 2) mole-
cules with relatively few atoms and a well-resolved
vibrational–rotational structure; 3) complex molecules.
The problem has been solved in practice for molecules
of type 1) but, in many cases, only the principle has
been established for molecules of type 2), and the prob-
lem has not yet been solved at all for molecules of type
3).

The detection of traces of simple molecules which
have sharp electronic absorption lines in the visible and
ultraviolet range can be performed most effectively by
the fluorescence method. In principle, this method
should make it possible to attain quite readily the ulti-
mate sensitivity corresponding to single molecules in
one vibrational–rotational state. However, the majori-
ty of molecules does not have sharp electronic lines in
the gaseous phase. For some classes of molecules
(aromatic hydrocarbons), it is possible to obtain nar-
row fluorescence lines at low temperatures in frozen
matrices (Shpol'skiĭ effect[155]). It has been established
recently that Shpol'skii effect occurs in many molecules
but, under normal experimental conditions, it is not
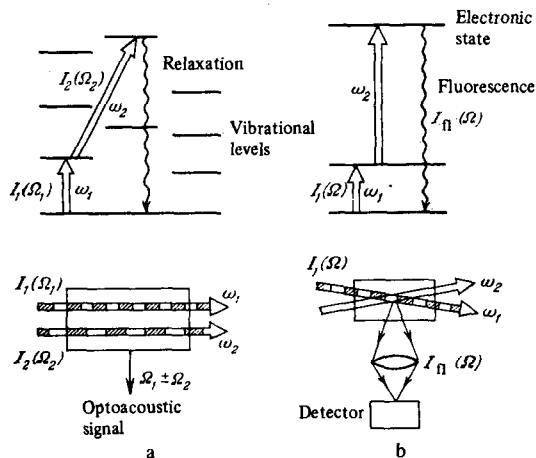observed because of the inhomogeneous broadening of

FIG. 15. Enhancement of the selectivity of the optoacoustic (a)
and fluorescence (b) methods for detection of molecules with
the aid of intensity-modulated excitation of an intermediate
vibrational level.

the spectral lines of molecules in frozen solutions.[156]
Monochromatic laser excitation of solutions of mole-
cules at low temperatures very often produces narrow-
band fluorescence which can be used for the selective
detection of many molecules in low concentrations. In
particular, this applies to the detection of traces of
some strongly carcinogenic hydrocarbons in air.

The detection of more complex molecules for which
narrow electronic absorption and fluorescence lines
are not known has to be carried out using the vibra-
tional–rotational spectra in the infrared range. In the
case of molecules with well-resolved vibrational–rota-
tional structures, we can use the absorption and opto-
acoustic methods. In this way, we can detect various
molecules which are present in the exhaust gases of
internal combustion engines.[8,9] The ultimate sensitivi-
ty of these methods (Table 1) lies in the range 10^{10}
molecules/cm^3, i.e., it is of the order of 0.1 – 1 ppb.
However, the main difficulty in the practical realization
of such sensitivity is the weak background absorption of
the medium which gives rise to a signal that is indistin-
guishable from the signal of the molecules being inves-
tigated. Therefore, the ultimate sensitivity reached
under laboratory conditions in the detection of mole-
cules in a pure medium such as an inert gas is not at-
tainable when the same molecules are being detected in
the atmosphere. The situation is further complicated
by the fact that the weak absorption of air and its im-
purities has not yet been investigated in the infrared
range at the absorption level of 10^{-6}–10^{-8} cm^{-1}.

Therefore, the selective detection of molecules of
type 2) necessitates improving considerably the meth-
ods described above so as to increase their sensitivity.
One of the possible improvements of the optoacoustic
method is shown in Fig. 15a. The idea is to excite
selectively a vibrational level of energy $\hbar\omega_1$ and then
excite a higher vibrational level of energy $\hbar(\omega_1 + \omega_2)$ by
additional infrared radiation. The intensity of each of
these radiations is modulated at different acoustic fre-
quencies Ω_1 and Ω_2. The unavoidable background ab-

sorption by other molecules, whose absorption lines are located at frequencies ω_1 and ω_2, gives rise to opto-acoustic signals at the acoustic frequencies Ω_1 and Ω_2 which are indistinguishable from the signals of the molecules being detected. However, the two-step excitation of the molecules being detected should give rise to an optoacoustic signal at frequencies $\Omega_1 \pm \Omega_2$, which can only be due to the molecules that have two vibrational transitions with the same frequencies. The probability of such coincidences is much less likely than the coincidence with one absorption line. Therefore, this method should be more selective but it requires, firstly, the knowledge of the vibrational spectra of the transitions between excited vibrational levels of the molecules being detected and, secondly, it requires saturation of the absorption at the first vibrational transition characterized by the energy $\hbar\omega_1$.

Two-step excitation may also increase considerably the sensitivity of selective detection of complex molecules which exhibit wide-band fluorescence. Let, for example, infrared laser radiation modulated at a frequency Ω be used to excite a vibrational level of a molecule (Fig. 15b). Excitation by ultraviolet radiation ω_2 of an electronic fluorescence state of the molecule results in the excitation of some of the molecules from the vibrational level and, consequently, gives rise to a fluorescence modulated at the frequency Ω. If the dependence of the intensity of the modulated frequency is determined as a function of the infrared radiation frequency ω_1, molecules with certain vibrational bands can be detected. This absorption-fluorescence spectroscopy, utilizing the method of double infrared-ultraviolet resonance, combines the selectivity of infrared spectroscopy and the sensitivity of the ultraviolet fluorescence method.

However, all these methods fail to solve the problem of selective detection of complex type 3) molecules in mixtures. Many complex molecules have vibrational-rotational structures which cannot be resolved by the linear spectroscopy methods. For example, complex hydrocarbons have continuous vibrational bands which differ little from one another when the molecular structure is altered. The problem of selective excitation of such molecules by the linear spectroscopy methods cannot be solved even in principle. At present, such molecules are being identified by mass spectroscopic analysis in combination with chemical analytic methods. However, one can already see how laser spectroscopy can provide physical methods for the detection and identification of complex molecules.

The greatest hope lies in the methods of nonlinear spectroscopy free of the Doppler broadening, which should increase the spectral information and the degree of selectivity by a factor of 10^3–10^5 (Sec. 4). The first experiments involving qualitative analysis of hydrocarbons by the absorption saturation methods [128] have demonstrated the promising nature of such applications.

Another possible way of increasing the sensitivity and selectivity of the detection of complex molecules can be based on the use of laser radiation in mass spectroscopy. The selective ionization of molecules by laser
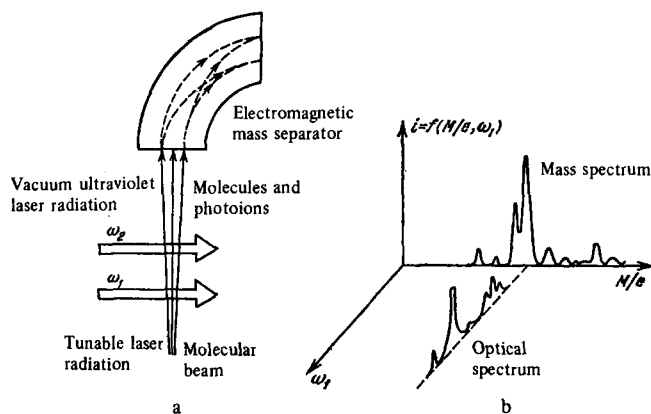

FIG. 16. Laser mass spectrometer based on selective two-step photoionization of molecules by laser radiation: a) possible configuration; b) two-dimensional spectrum (infrared absorption and mass spectrum).

radiation can provide the basis for a laser mass spectrometer, the idea for which is illustrated in Fig. 16. A tunable laser emitting at a frequency ω_1 excites selectively a vibrational (or sometimes electronic) state of a molecule. This excitation shifts by a small amount the photoionization band edge, which usually lies in the vacuum ultraviolet. A second laser emitting in the vacuum ultraviolet photoionizes the molecule and the frequency of this laser is chosen to lie in the region of the steepest slope of the photoionization band edge. A preliminary selective excitation of molecules by a tunable laser provides only a low energy $E_{exc} \approx 0.1$–0.5 eV but alters considerably (by 10^{-1}–$10^{-2}\%$, if allowance is made for the distribution of the molecules between the rotational states) the photoionization cross section, i.e., it alters the photocurrent. Photoions are directed to a conventional mass spectrometer, which is used to measure the mass spectrum, i.e., the dependence $i = f(M/e)$. In this variant, it is possible to measure the photocurrent for a given value of M/e as a function of the tunable laser frequency. This system should make it possible to determine the infrared spectrum of a microscopic amount of complex molecules because, when the frequency ω_1 coincides with the absorption frequency of the molecule, molecules are transferred to an excited state, and, consequently, the ion photocurrent amplitude changes. Thus, a laser mass spectrometer with a selective ionization of molecules instead of the usual nonselective ionization by an electron beam (or continuous vacuum ultraviolet radiation) should yield both the optical (infrared and visible) absorption spectrum and the mass spectrum (Fig. 16b). This method can be used to obtain information on the spatial structure of different molecules with the same mass, etc. The first successful experiments on the photoionization of molecules were reported in [157]; they were carried out using a simple and practical vacuum ultraviolet H_2 laser emitting at 1550 Å and 1200 Å [47] and they demonstrated the feasibility of such laser selective detectors of complex molecules.

We are approaching here the fundamental problem of the development of physical methods for the detection

and identification of small amounts of organic impurities with a precision which is attainable in the olfactory organs of man and animals. Physics has given us instruments which are much more sensitive than other senses with one exception, the sense of smell. P. L. Kapitsa said that "one of the tasks for the physics of the future is to catch up with the smell of the dog."[158] The methods of laser spectroscopy mentioned above and those still to be developed should play an important role in solving this problem.

C. Remote detection of atoms and molecules

Remote detection of atoms and molecules in the atmosphere or even in the ionosphere is one of the most important practical tasks of laser spectroscopy. Instruments for qualitative and quantitative determination of the atmospheric composition, usually called lidars, are combinations of laser rangefinders (optical radars) and laser spectrometers. Lidar operation is based on the transmission of a laser pulse to some remote region containing the particles to be detected and the reception of a small part of this pulse returned from this region. The radiation returns because of the resonance, Raman, and Rayleigh scattering. The first two types of scattering can be used directly in the determination of the nature of the scattering particles, whereas the Rayleigh scattering only gives an interfering background. However, the Rayleigh back-scattering in combination with resonance absorption by the particles being detected is also suitable for remote selective detection of particles.

The status of the remote detection of molecules by the inverse Raman scattering was reviewed in the present journal[133] and will not be discussed here. By way of illustration of the effectiveness of the resonance fluorescence method, we may mention an investigation[14] in which a flashlamp-pumped pulse dye laser emitting only 2 mJ at the Na D lines was used to detect Na vapor in the upper atmosphere at altitudes of about 90 km. Systematic measurements yielded concentrations of Na atoms of about 10^3 atoms/cm^3.[159] This method can be used to detect other atoms, ions, and molecules in the upper atmosphere but it would require dye lasers emitting pulses of higher energy. In particular, it should be possible to detect the presence of OH radicals, which play an important role in the chemistry of the atmosphere.

8. SPECTROSCOPY OF EXCITED STATES

Laser radiation can be used to excite a selected electronic state of an atom or a rovibronic state of a molecule and then to determine the time and channels of the relaxation from the excited to the ground state, as well as quantum transitions to other lower states. Essentially, the first methods for systematic investigations of excited states of atoms and, particularly, of molecules appeared only since the advent of the laser. The generation of short light pulses of durations down to 10^{-12} sec has provided experimenters with very effective methods for the direct study of ultrafast molecular processes with picosecond resolution, about which only hypotheses were made a few years ago. The spectros-

copy of excited states of atoms and molecules is a rapidly growing branch of laser spectroscopy, closely related to the selective interaction of laser radiation with matter, such as that used in the laser separation of isotopes. Information on the relaxation of excited states of molecules is of exceptional interest in chemistry and biology. We may expect a very rapid and productive growth of laser spectroscopy of excited states of atoms and molecules. The next few pages are intended simply as an illustration of the great potentialities of this branch of laser spectroscopy.

A. High atomic states

Systematic investigations of high states of even simple alkali atoms with one optical electron are seriously hindered by the complexity of the method needed to excite them. For example, the excitation of S levels is difficult because this cannot be done directly from the ground state. Selective excitation by resonance or laser radiation of atoms to an intermediate state and subsequent selective excitation by a tunable laser to higher states removes almost completely these difficulties. This approach makes it possible to investigate almost any atomic levels. At this stage, the greatest interest lies in the simplest atomic structures, such as those of alkali atoms, because the fullest theoretical interpretation can be made of the results.

Experiments usually involve the excitation of atoms to higher S and D states with $n \gg 1$ by dye laser radiation from the first excited states, which are populated by the radiation of a second dye laser (sometimes by the resonance radiation of a spectroscopic lamp). The following types of experiment were successfully performed on higher excited states of alkali atoms:

1) the level crossing effect and the Hanle effect were investigated in a weak magnetic field in[160] and the results gave the values of the hyperfine splitting and the Landé g factor of the states;

2) autoionization in a weak external electric field was studied[161,162] and this made it possible to increase considerably the cross section for the selective laser photoionization of atoms;

3) quantum beats of the intensity of the spontaneous radiation originating from higher excited states were observed in[163] and this made it possible to investigate the fine structure of the levels masked by the Doppler broadening;

4) excitation was transferred between higher states with different angular momenta in[164] (the radius of an atom excited to a state $n \gg 1$ increases proportionally to n^2 so that the state with $n \gg 1$ has an exceptionally large collisional cross section).

B. High vibrational states of molecules

The selective excitation of molecular states makes it possible to determine the rates of transfer of energy, of chemical reactions of excited molecules, and of nonradiative transitions in molecules. It is important to know the rates of the processes involving molecules in specific rotational, vibrational, and electronic quantum
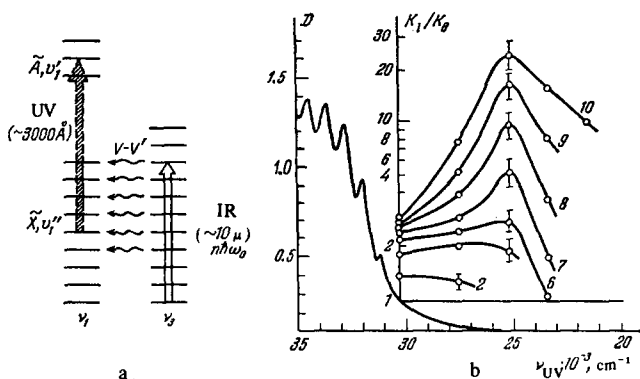
FIG. 17. Direct observation of highly excited vibrational levels of the OsO_4 molecule: a) transitions participating in multiphoton infrared excitation and ultraviolet absorption; b) changes in the electronic absorption spectrum at different intensities of exciting CO_2 laser radiation (numbers alongside the curves give the power density in MW/cm^2, D is the optical density, K_I is the absorption coefficient under laser excitation conditions, and K_0 is the absorption coefficient in the absence of excitation).[168]

states to understand the elementary processes in chemical kinetics. This aspect of the laser spectroscopy methods is discussed in[11,12]. Here, one should mention the recently reported possibility of investigating higher vibrational states of polyatomic molecules.

Ambartsumyan *et al.*[165,166] discovered the isotopically selective dissociation of molecules by a resonant infrared laser field of 10^8–10^9 W/cm^2 power (this was done on BCl_3 [165] and SF_6, [166] and on other molecules). This phenomenon immediately attracted the attention of many laboratories[167] because it made it possible to develop relatively simple and technologically acceptable methods for the separation of isotopes of many elements by the cheap and widely accessible method of pulse CO_2 laser radiation. Moreover, this effect provided the first means for investigating resonant multiphoton absorption in vibrational transitions in molecules and selective excitation of higher vibrational states. A direct observation of nonequilibrium excitation of higher vibrational states in the OsO_4 molecule was reported recently[168] after multiphoton absorption of CO_2 laser radiation of 10.6 μ wavelength. In this study, use was made of the double infrared-ultraviolet resonance method developed in[169,170] in which the vibrational state of the molecules was absorption-probed by an ultraviolet beam using a transition to an excited electronic state. The same method was used in a detailed study of the relaxation processes in the NH_3 molecule in $N^{14}H_3 + N^{15}H_3$ mixtures in the course of an investigation which resulted in the first successful separation of isotopes by the method of two-step selective laser photodissociation of molecules. [171]

Figure 17a shows schematically the process of excitation of the ν_3 vibration of the OsO_4 molecule and the probing of the population of the vibrational levels of the ν_1 mode by ultraviolet absorption (the ν_3 modes does not appear in the ultraviolet spectrum). The nature of the deformation of the $v_1'\tilde{A} - v_1''\tilde{X}$ electronic absorption band is shown in Fig. 17b. The absorption band edge

shifts in the direction of longer wavelengths and the amount of the shift depends strongly on the intensity of a CO_2 laser pulse. The deformation of the band corresponds to a nonequilibrium population of the higher vibrational levels and the kinetics of the filling of the levels can be deduced from the shape of the ultraviolet absorption pulse. A change in the electronic absorption spectrum occurs only after the V–V′ exchange of excitation between the modes ν_3 and ν_1, ν_2, ν_4. The independence of the shape of the electronic absorption pulse of the ultraviolet wavelength was taken in[168] to indicate that higher vibrational levels were populated immediately. The maximum measured shift of the red edge of the absorption band was $\Delta\nu_s \approx 10^4$ cm^{-1}, which indicated that the V–V′ exchange was followed by the population of the levels with $v''(\nu_1) \approx \Delta\nu_s/\nu_{1as} \approx 10$. Hence, it was concluded that multiphoton absorption of infrared laser radiation filled the vibrational levels of the ν_3 mode whose energy was several times greater than $\hbar\omega_1[v''(\nu_1)] \approx 1$ eV.

A combination of the multiphoton excitation of the molecular vibrations and the investigation of their excited states on the basis of changes in the ultraviolet spectrum is likely to develop into a promising branch of spectroscopy of high vibrational states of polyatomic molecules which have never been studied before.

C. Picosecond spectroscopy of excited molecules

Until recently, it was possible to measure atomic and molecular processes with a temporal resolution of the order of a nanosecond because the resolution limit was governed by the response time of light sources and of the photoelectronic radiation detectors. The fairly large number of fast processes could be studied only by indirect methods. In the last few years, an extremely effective method has been developed for the control of the radiation emitted by multimode solid-state pulse lasers—the method of mode locking in a nonlinear absorber—which makes it possible to produce a train of several tens of very short pulses of 10^{-11}–10^{-12} sec duration and 10^8–10^9 W peak power.[172] Details of the mechanism of the formation of such ultrashort pulses and of their uses can be found in.[173,174] These ultrashort pulses provide the experimental base for the development of several effective picosecond spectroscopy methods which are growing rapidly and have already been used in several fundamental experiments on complex molecules. The first few experiments and the picosecond spectroscopy methods are described in[13,175]. The latest achievements of picosecond spectroscopy and its applications to chemical and biological systems in solutions are reviewed in[176].

In all the methods of selective excitation of electronic or vibrational states, use is made of a high-power picosecond pulse and several methods are employed to observe relaxation and excitation transfer processes:

1) the method of a test picosecond pulse used to probe the absorption at the excitation wavelength[177] or at other wavelengths[178];
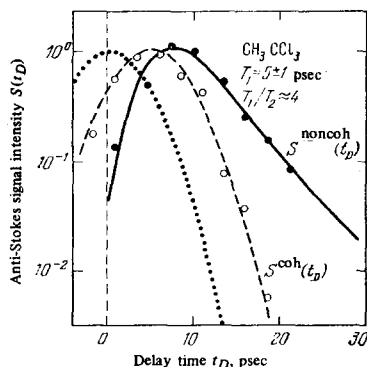
2) the method of observation of the kinetics of spon-

FIG. 18. Intensities of coherently and noncoherently scattered probing ultrashort pulses plotted as a function of the delay time t_D, obtained in a study of the symmetric vibration of the CH_3 valence bond at 2900 cm^{-1} in the CH_3CCl_3 molecule.[185]

taneous radiation with the aid of an optical Kerr shutter controlled by a picosecond pulse[179] or with an image-converter camera capable of picosecond resolution[180];

3) the method of stimulated Raman scattering for the excitation and investigation of the relaxation of the vibrational states of molecules. [181]

The most striking example of the effectiveness of these methods is the recent direct measurement of the relaxation of the electronic excitation of a polyatomic molecule in the absence of collisions. Theoretical ideas (see[182]) show that large polyatomic molecules may relax nonradiatively even in the absence of collisions. Proof of this statement is the observation that a complex molecule excited to a state above the first singlet level very rarely emits radiation, i.e., it usually relaxes nonradiatively to the ground state. This applies also the molecules in the gaseous phase, [182,183] which is considered to be the main indirect proof of the collisionless relaxation of the excitation of complex molecules. A fast nonradiative picosecond relaxation of two large polyatomic molecules (perylene and di-methyl POPOP) in the gaseous phase was observed directly in[184]. The molecules were excited by the third harmonic (353 nm) of ultrashort neodymium-glass laser pulses and fluorescence was recorded with an image converter camera with a temporal resolution of 15 psec. It was found that the radiative relaxation time in the absence of collisions was shorter than 30 psec in both cases. This method provides a powerful experimental means for the direct study of intramolecular processes in complex molecules about which much is still unknown and unclear.

In the picosecond spectroscopy of excited vibrational levels of molecules in the ground electronic state, the most effective method is the Raman scattering based on the excitation of molecular vibrations by the stimulated Raman effect and probing of the state of the excited molecular vibrations by observing coherent (directional) and noncoherent (isotropic) spontaneous Raman scattering of an additional picosecond laser pulse by these vibrations. This method is a variant of the active Raman spectroscopy method discussed above in Sec. 5. The time T_2 needed for the loss of phase locking can be

measured by recording the dependence of the intensity of the coherent anti-Stokes scattering on the delay time relative to the ultrashort laser pulse exciting molecular vibrations. The relaxation time of the population of the vibrational level T_1 can be found by recording nondirectional noncoherent scattered radiation at the anti-Stokes frequency. Systematic measurements of the vibrational relaxation of molecules were carried out by Kaĭzer et al.[181,185] using this method, and by Alfano and Shapiro.[186,187] The results of the experiments carried out on the CH_3CCl_3 molecule are plotted in Fig. 18. Separate measurements of the coherently and noncoherently scattered light gave values of the phase-locking relaxation time T_2 and of the vibrational energy relaxation time T_1. A similar method was used in a study of the intramolecular and intermolecular types of decay of the vibrational excitation. For example, the relaxation of the 2900 cm^{-1} vibrations in pure CH_3CCl_3 and $C_2H_5 \cdot OH$ liquids was found to occur mainly by decay to vibrations with half the energy.[185,187] This process was deduced from the appearance of the anti-Stokes noncoherent scattering with a shift to a frequency different from that of the excited vibration. An analogous method was used in the detection of the transfer of the vibrational energy from the CH_3CCl_3 to the CD_3OD molecules in their mixture.[185]

The method of Raman scattering of picosecond pulses can also be used in the direct measurement of the relaxation of elementary excitations (optical phonons, [186] polaritons, etc.) in a solid.

Thus, several effective picosecond spectrometry methods are available for investigation of the rates and mechanisms of the relaxation of the vibrational and electronic energies of polyatomic molecules and this should help in understanding the molecular structure.

9. CONCLUSIONS

This series of brief sketches of the current status, principal directions, and potential developments in laser spectroscopy should be concluded by pointing out two subjects mentioned in the Introduction but not considered further. One of them is the active laser spectroscopy, which lies at the interface between quantum electronics, optical spectroscopy, and photochemistry.

Many of the laser spectroscopy methods described above have originated from the development of new methods for selective action of laser radiation on matter. This problem deserves a separate review. However, the interested reader may turn to the reviews in[154,188] in which the application of the selective interaction to isotope separation is considered. Another subject is the laser-nuclear spectroscopy, which is at the interface between optical and nuclear spectroscopic studies. For the status of this subject, which deserves a separate review, the reader is directed to[189,190].

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