Nonlinear High Resolution Laser Spectroscopy

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The laser is a source of coherent optical radiation of extraordinarily wide usefulness in fundamental research and technology. Its application in optical spectroscopy is an excellent example of this.

Laser spectroscopy has made it possible to study, and in some cases to solve, a number of fundamental problems which could not be investigated by classical spectroscopy. Some features of laser spectroscopy related to such problems are:

1) A limit of resolution which is determined by the width of the spectral lines of the substance rather than by the instrumental width of the spectral apparatus. This is of special importance for gas spectroscopy in the infrared region, where a resolution of about 0.01 cm^{-1} could otherwise be reached only with unique apparatus, while the resolution obtained with the best commercial devices is about 0.1 cm^{-1}, or 10^2 times the Doppler width.

2) Elimination of Doppler broadening in atomic and molecular spectroscopy with gaseous samples. A highly coherent beam of laser light forms the basis for the methods of nonlinear spectroscopy, with which one can study the spectral line structure that is usually screened by Doppler broadening due to the thermal motion of the particles (*1–3*). A resolving power up to about 10^{10} can be achieved experimentally.

3) Extreme sensitivity in atomic and molecular spectral analysis. With laser radiation it is now possible to record about 10^2 atoms per cubic centimeter [fluorescence of sodium vapor excited by a tunable visible laser (*4*)] or 10^{10} molecules per cubic centimeter [optoacoustic detection by a tunable infrared laser (*5, 6*)]. Methods have been proposed for using lasers to detect selectively single atoms and molecules (*7*) and to reach a sensitivity obtainable with the best mass spectrometers. However, the methods of laser spectroscopy, as opposed to those of mass spectroscopy, can detect not only the type of particle but also its quantum (electronic, vibrational, and rotational) state.

4) Selective excitation of atomic and molecular states. Laser radiation can excite a considerable portion of the atoms and molecules in a sample to a particular quantum state, and their modes of relaxation to the ground state (*8*) or quantum transitions between excited states can be traced. Ultrashort light pulses make it possible to measure directly the relaxation time of excited molecules in a condensed medium (*9*).

5) Remote spectral analysis. Pulses of collimated coherent radiation can excite Raman and resonance scattering and fluorescence of atoms and molecules at great distances [up to hundreds of kilometers away (*10*)], yielding information on atomic and molecular composition. These methods are of importance for atmospheric and air pollution control studies (*6*).

6) Local spectral analysis. By focusing laser radiation one can perform spectral analysis on a substance localized in a small volume, down to the dimensions of a wavelength cubed. This has been done in local emission spectral analysis (*11*). The potential of local spectral analysis is greatest in medicine and biology.

I wish to stress that the scope of laser spectroscopy is much greater than that of traditional spectroscopy for studies of the composition and structure of matter. With laser radiation, using the selectivity of light absorption by a substance, it is possible to change the composition and properties of the substance (*12*). This is sometimes called "active" laser spectroscopy. In the broad sense laser spectroscopy is an intermediate link in the chain of practical and fundamental applications of coherent light in chemistry, biology, and other fields.

In this article I consider the state and prospects of nonlinear, extremely high resolution laser spectroscopy. Thus, only problems related to the second feature listed above are dealt with here. In 1972 Brewer (*1*) discussed one of the methods of nonlinear, high resolution laser spectroscopy, namely absorption saturation, which was the dominant method at that time. Considerable progress has been made in the last few years, and the problem can be treated from a more general point of view.

Infrared High Resolution Spectroscopy

The methods of infrared spectroscopy can be conditionally divided into three classes, as outlined in Table 1: classical (linear) spectroscopy, linear laser spectroscopy, and nonlinear laser spectroscopy without Doppler broadening. The methods and apparatus of classical spectroscopy furnish a resolution for absorption and emission lines of about 0.01 cm^{-1}, which is about an order of magnitude greater than the Doppler width of spectral lines in a gas. In order to obtain a spectrum in the neighborhood of strong absorption lines of a gas, the sample cell should contain, as a rule, at least 10^{18} molecules, and with weaker absorption lines a proportionally greater number of molecules is needed. Classical spectroscopy furnishes data on the absorption and emission of light by a molecular gas over a wide wavelength range, but it is not very useful for studying the shape and small splittings of spectral lines.

Laser linear spectroscopy (*6*), using infrared lasers with a narrow line and tunable frequency, is similar to molecular radio spectroscopy with tunable microwave oscillators. In the infrared the laser plays the same role as the klystron in radio spectroscopy. In linear laser spectroscopy one can study the shapes of spectral lines and line splittings due to various effects. Specifically, isotope line shifts and the broadening and narrowing of spectral lines of a gas caused by intermolecular collisions can be measured. For a line at wave number ν_0 in a gas, the Doppler broadening is usually 10^{-5} to 10^{-6} ν_0. Therefore, a laser spectrometer with a resolving power of about 10^6 can precisely measure the spectral line shape, but not the line structure, which is screened because of the molecules' thermal motion. However, the Doppler width can be substantially reduced if atomic or molecular beams are used (*13*). More important may be the development of highly sensitive laser techniques for detecting weak infrared absorption signals; for example, using the optoacoustic effect or the derivative signal recording it is possible to obtain the spectrum of a sample containing only 10^{10} molecules (*5*). This has opened the way for using infrared extremely high resolution spectroscopy to detect trace amounts of molecules in a gas (*6*).

The narrowness (high monochromaticity) of laser radiation is used in nonlinear spectroscopy to study the structure of absorption lines. With new experimental methods a resolving power of up to 10^{11} is

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available, so that line splittings of 10^{-5} times the Doppler width can be resolved, and the sensitivity is at least comparable with that of linear methods. Thus, the nonlinear laser techniques with which we are concerned in this article give a resolving power 10^6 times more and a sensitivity 10^7 times more than those of classical infrared spectroscopy.

Three fundamentally different approaches are used in nonlinear laser spectroscopy without Doppler broadening. These are outlined below and in Table 2, and described in greater detail in the following sections.

1) Saturation spectroscopy is based on the changes in the velocity distribution of atoms or molecules excited from the ground state to a higher energy state by a coherent light wave.

2) Two-photon spectroscopy is based on the simultaneous absorption of photons from two laser beams similar in frequency but traveling in opposite directions.

3) Trapped particle spectroscopy is based on changes in the velocity distribution of atoms or molecules confined to oscillatory motions in a strong, nonresonant light beam.

Table 1. Methods of infrared high resolution spectroscopy. The sensitivity is the number of molecules in the sample.

Method	Resolving power	Sensitivity	Application
Conventional (linear) spectroscopy	10^5	10^{18}	Absorption and emission spectra in a wide wavelength range
Linear laser spectroscopy	10^5 to 10^7	10^{10}	Structure and shape of absorption lines of gases. Detection of trace amounts of molecules in a gas
Nonlinear laser spectroscopy	10^6 to 10^{11}	10^{10}	Spectroscopy of gases at low pressure without Doppler broadening

Table 2. Methods of nonlinear laser spectroscopy without Doppler broadening.

Method	Physical phenomenon	Author
Saturation spectroscopy	Change of the velocity distribution of atoms or molecules at the quantum levels of a saturated transition	Lamb, 1962–1964 (*15*)
Two-photon spectroscopy	Compensation of Doppler shift by the simultaneous absorption of photons from counterrunning light waves	Vasilenko *et al.*, 1970 (*32*)
Trapped particle spectroscopy	Oscillatory motion of slow particles in a strong standing light wave (trapping of atoms or molecules)	Letokhov, 1968 (*38*)

Saturation Spectroscopy

A Doppler-broadened spectral line is a complex of a great number of much narrower lines corresponding to molecules with different thermal velocities, **v**. This is why the Doppler effect on spectral lines is often called inhomogeneous broadening. The natural line width is referred to as the homogeneous width, 2Γ. A coherent light wave of wave vector **k** interacts only with the particles it resonates with—that is, with particles for which the Doppler shift in the absorption frequency, $\mathbf{k}\cdot\mathbf{v}$, compensates precisely for the detuning of the field frequency, ω, with respect to the transition frequency, ω_0, of a fixed molecule. The proportion of molecules that interact with the field depends on the ratio of the homogeneous width to the Doppler width in the equilibrium velocity distribution. Assume that the laser light is intense enough to stimulate transitions of a considerable proportion of the molecules to an excited state. The excitation of particles with a certain velocity changes the equilibrium distribution of particle velocities on each level of the transition (Fig. 1). On the lower level there is a lack of particles whose velocity complies with the resonance condition—that is, a hole in the velocity distribution. By contrast, on the upper level there is an excess of particles with resonance velocities, or a peak in the velocity distribution. The hole depth and peak height depend on the degree of absorption saturation by the light field. Thus, a light wave changes the velocity distribution of molecules on both levels, and the distributions become nonisotropic. This brings about a distortion of Doppler-broadened absorption or emission lines. Because some of the molecules have passed into an excited state a hole, which is often called a Bennett hole, arises in the Doppler-broadened line profile (*14*). The width of the hole determines the homogeneous line width, which can be thousands of times less than the Doppler width.

A related phenomenon known as the Lamb dip forms the basis for many experiments in saturation spectroscopy. Consider the interaction of a Doppler-broadened line with a standing light wave. It is precisely such a field that is usually present inside a laser, and it can be considered as a superposition of two counterrunning light waves of the same frequency (Fig. 2). In this case each wave burns its own hole in the molecular velocity distribution, and since the two light waves are directed toward each other the two holes are symmetric about the center of the Doppler profile. In essence, the laser field extracts energy from two groups of particles with different velocities. When the laser frequency is tuned to the center of the Doppler profile both holes coincide, and the standing light wave interacts with only one group of par-

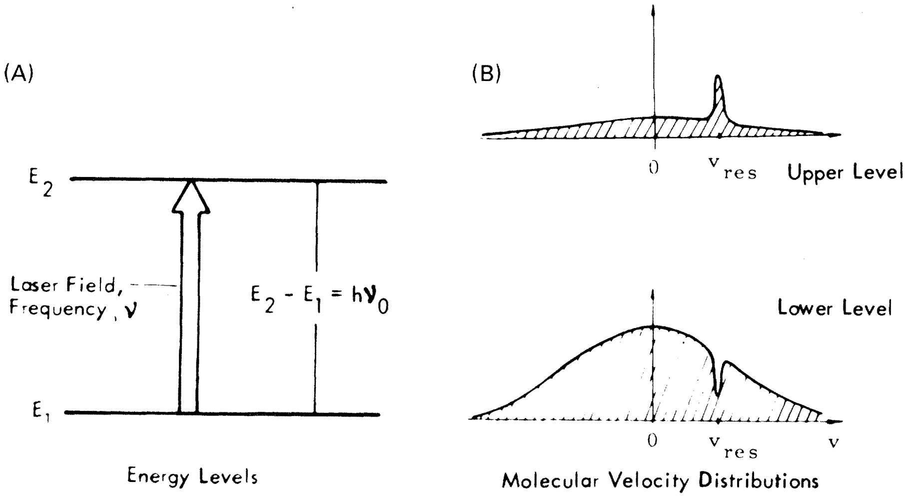


Fig. 1. Changes in the particle velocity distribution over two levels of a transition under the action of a laser wave of frequency ν. The Z-component of velocity of the particles interacting with the light wave is $v_{\text{res}} = c(\nu - \nu_0)/\nu_0$.

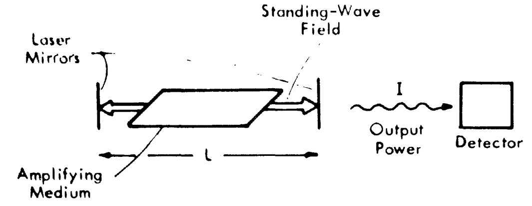
ticles, producing a resonance dip in the output power of the laser at the center of the amplification line. This effect was first investigated by Lamb in 1962–1964 (*15*) in his gas laser theory, and was confirmed experimentally by two independent groups (*16, 17*).

The saturation method, which led to wide use of the absorption method, was further modified in 1967 at three different laboratories (*18–20*) by the addition of a gas resonant-absorption cell at low pressure located inside the laser cavity. The absorption saturation in the standing light wave gives rise to a narrow Lamb dip at the center of the Doppler-broadened absorption line. Total saturated amplification of the two-component medium inside the laser results in a narrow peak at the center of the absorption line and in the output power of the laser, which is referred to as an inverted Lamb dip. Barger and Hall (*21*) first successfully observed the inverted Lamb dip by use of a molecular absorption cell. Of course, the molecular cell does not have to be inside the laser resonator. A standing wave of the desired intensity can be produced outside the resonator by use of an additional mirror. A valuable feature of the inverted Lamb dip is that it can be used to study any Doppler-broadened absorption, provided coherent, narrow-line laser radiation is available at the transition frequency.

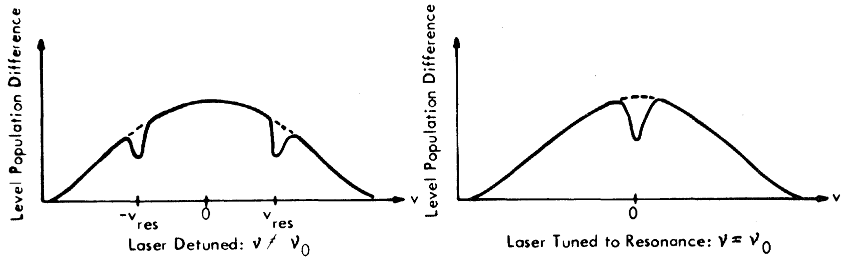
Table 3. Methods of saturation spectroscopy.

Method	Proposal	Experiment
Lamb dip	Lamb, 1962–1964 (*15*)	Szöke and Javan, 1963 (*16*); McFarlane *et al.*, 1963 (*17*)
Inverted Lamb dip	Letokhov, 1967 (*18*); Lee and Skolnick, 1967 (*19*)	Lee and Skolnick, 1967 (*19*); Lisitsyn and Chebotaev, 1968 (*20*)
Dip with counter-running probe wave	Letokhov and Chebotaev, 1969 (*22*)	Basov *et al.*, 1969 (*23*)
Dips at coupled transitions	Schlossberg and Javan, 1966 (*24*)	Schlossberg and Javan, 1966 (*25*)
Dip of total level population (fluorescence dip)	Basov and Letokhov, 1968 (*30*)	Freed and Javan, 1970 (*31*)

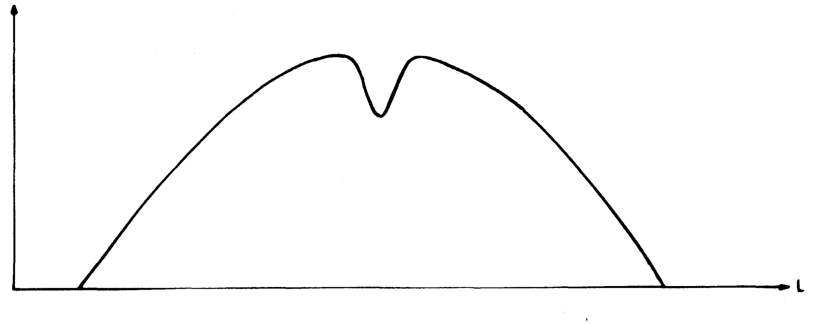
To obtain a narrow, nonlinear resonance at the center of an absorption line it is not necessary to use a standing light wave. It is sufficient to have one strong traveling wave saturating the absorption and a weak wave traveling in the opposite direction acting as a probe wave (Fig. 3) (*22*). The molecules whose velocity, $\mathbf{v}_{\text{res}}$, complies with the resonance condition, $\mathbf{k}\cdot\mathbf{v}_{\text{res}} = \omega - \omega_0$, are excited by the strong traveling wave. Since the probe wave has the same frequency but is opposite in direction, it interacts only with molecules whose velocity is the same in magnitude but opposite in direction to that of molecules that interact with the saturating wave. If the wave frequency and ω_0 coincide, the probe wave interacts with the molecules whose absorption is already reduced by the saturating wave. As a result the probe wave absorption has a resonance minimum similar in width to the homogeneous width and placed exactly at the center of the Doppler-broadened line. Basov *et al.* (*23*) did the first experiments on spec-



(a) Lamb-Dip Experiment



(b) Velocity Distribution Curves



(c) Power Output Curve

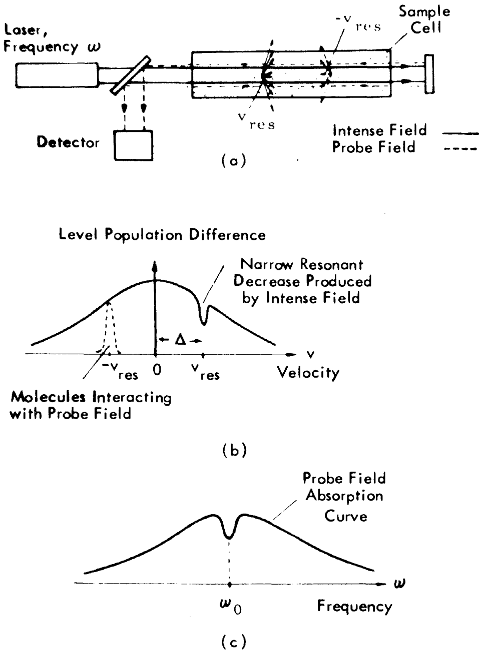


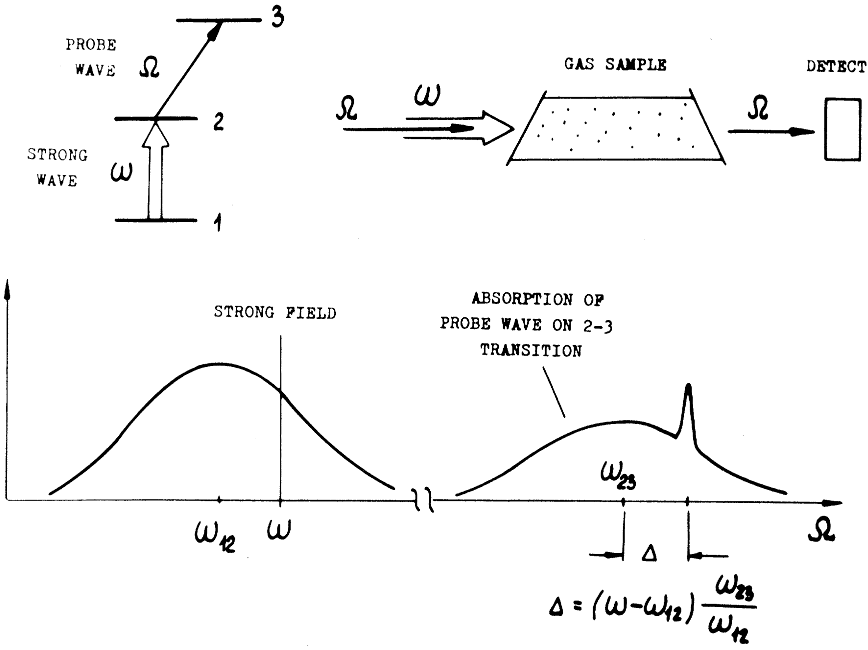
Fig. 2 (left). Formation of a Lamb dip in the laser output power when the oscillation frequency ν is scanned through the Doppler contour of amplification line. Fig. 3 (right). Absorption saturation spectroscopy with a counterrunning probe wave.

troscopy inside the Doppler line by this method.

The hole in the molecular velocity distribution that results when some molecules of a gas are stimulated into an excited state by a coherent light wave appears in coupled transitions as well. For example, because of the peak in the velocity distribution in the upper level (Fig. 1B) the line corresponding to transitions from this level to a still higher level will also have a resonance peak with a width much smaller than the Doppler width (Fig. 4). The line shape for a connected transition can conveniently be observed by use of an additional probe wave traveling in the same direction as the strong wave. This method for studying coupled transitions without Doppler broadening was first used by Schlossberg and Javan (*24, 25*). For infrared molecular spectroscopy it is of interest mostly for making precise measurements of small splittings, such as those caused by external fields, but it is applicable only to transitions with a common level.

For coupled atomic transitions, where the homogeneous line width depends mainly on radiative damping, nonlinear spectroscopy with a two-frequency field makes it possible to observe narrow resonances with line widths less than the homogeneous width. An atom absorbs photons $\hbar\omega$ and $h\Omega$ from two counterrunning waves of frequencies ω and Ω and makes a two-quantum transition from level 1 to level 3 (see Fig. 4) (*26, 27*). In this case the resonance width of the 2—3 transition is determined by levels 1 and 3 rather than by the initial and final levels. The contribution of level 2 is small if the difference between the two wave vectors is small. When $\mathbf{k}_\omega = \mathbf{k}_\Omega$ the resonance width is equal to the natural or radiative width of the 1—3 forbidden transition. Many effects in the three-level spectroscopy of two connected transitions have been discussed elsewhere (*28, 29*).

When the standing wave frequency is tuned to the center of a Doppler-broadened line, a resonant reduction in the saturated absorption is accompanied by a resonant change in the total number of particles on every level of a transition, regardless of their velocity (Fig. 5). There is a resonance minimum in the population of the upper level and a resonance peak in that of the lower level. This broadens the potential of saturation spectroscopy, since there are many efficient methods for detecting level populations, such as measuring the intensity of fluorescence from an



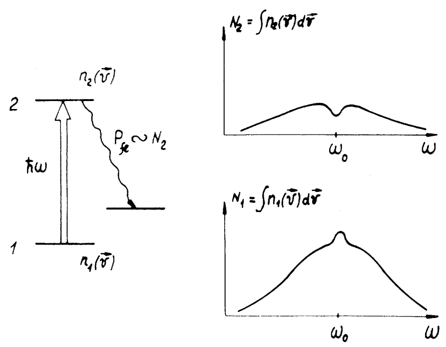
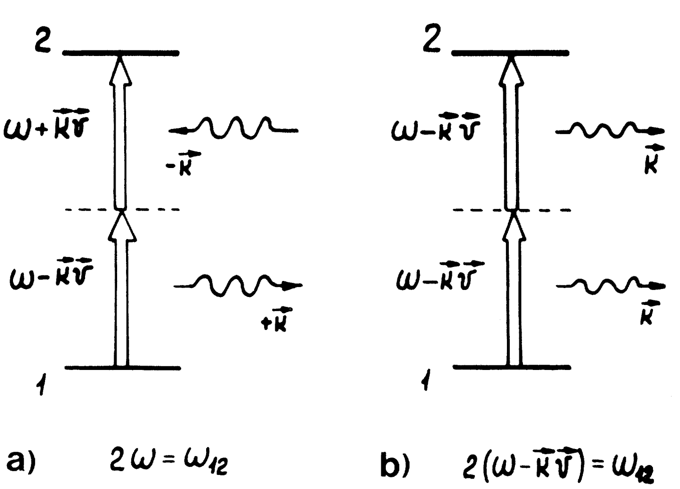


Fig. 4 (left). Absorption saturation spectroscopy at coupled transitions 1—2—3. Fig. 5 (right). Dip formation in the fluorescence intensity P_{fl} under a strong standing wave due to a dependence of the total number of excited particles N_2 from wave frequency ω.



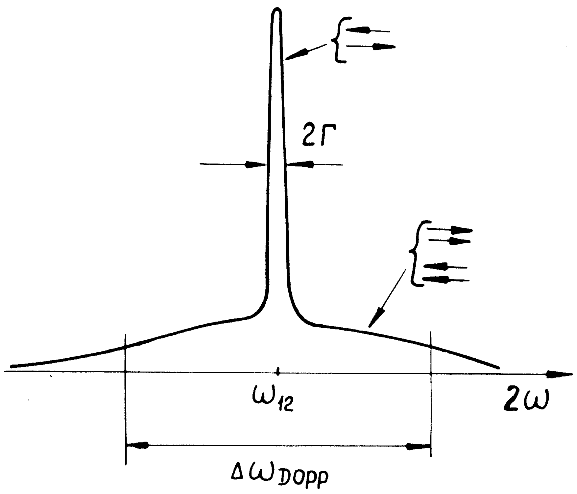


Fig. 6 (left). Compensation for the Doppler shift in the simultaneous absorption of two photons from two counterrunning waves (a) and the absence of compensation as photons from unidirectional waves are absorbed (b). Fig. 7 (right). Shape of a narrow resonance in two-photon absorption. The narrow resonance is caused by absorption of two photons from counterrunning waves, and the Doppler contour by absorption of photons from unidirectional waves.

excited state (*30, 31*). The high sensitivity of the method permits experiments at very low molecular gas pressures (below 10^{-3} torr) or even with molecular beams.

Table 3 summarizes the methods discussed in this section, including their authors and references for the first experiments. Saturation spectroscopy is the best developed area of nonlinear laser spectroscopy; it has been applied in dozens of experiments with atomic and molecular samples in many laboratories.

Two-Photon Spectroscopy

This technique was proposed by Chebotaev and co-workers (*32*). Consider a two-quantum atomic or molecular transition in the field of a standing wave of frequency ω (Fig. 6). For a particle moving with velocity $\mathbf{v}$ the frequency of traveling waves is $\omega \pm \mathbf{k} \cdot \mathbf{v}$. The only particles that can absorb two photons from one traveling wave are those for which $\mathbf{k} \cdot \mathbf{v}$ complies with the condition of two-photon resonance. However, simultaneous absorption of two photons from counterrunning waves is possible. In this case, the condition of two-photon resonance is only that the doubled field frequency coincides with the frequency of the two-quantum transition—that is, with the center of the Doppler-broadened line. In this type of resonance all particles, regardless of velocity, participate in two-photon absorption, resulting in a sharp increase of the absorption signal. The line shape of such absorption is shown in Fig. 7. It is the sum of a wide Doppler contour, representing two-quantum absorption from a unidirectional wave, and a narrow resonance, corresponding to two-quantum absorption by all particles for which $2\omega = \omega_0$. The amplitude of the resonance peak at the center of the line has a high contrast equal to the ratio of the Doppler width to the homogeneous width. Narrow two-photon resonances were first observed in 1974 in studies of sodium atom transitions in the visible (*33-35*).

I foresee rapid development of two-photon spectroscopy because it has several advantages compared to saturation spectroscopy. First, all the atoms take part in the absorption, regardless of their velocity, while in saturation spectroscopy only a small proportion of the atoms participate in the production of narrow resonances. For extremely narrow resonances the parameter $\Gamma/\Delta\omega_{\mathrm{Dopp}} \simeq 10^{-3}$ to 10^{-5}, so that the peak contrast is $\Delta\omega_{\mathrm{Dopp}}/\Gamma \simeq 10^3$ to 10^5 times as much as the Lamb dip contrast in saturation spectroscopy. Second, the two-photon absorption peak is accompanied by a corresponding peak in the density of excited particles. Since sensitive methods are available for detecting particles in the excited state, experiments can be conducted with a small number of particles, such as in beams. Third, the width of the resonance peak does not depend on the curvature of the wave front because the two photons are absorbed simultaneously at the same point in space. In absorption saturation, for narrow resonances to be attained, the wave vector should have strictly the same direction along the whole cross section of the standing wave. Thus, it is possible to use light beams with large cross sections (tens of centimeters) for two-photon spectroscopy, and broadening of the resonance peaks due to the motion of the atoms can be made very small. Indeed, the probability of a two-photon transition does not depend on the orientation of atomic velocities about the standing wave. Therefore, one can use an atomic beam moving along a standing wave and have a path length for the interaction of 100 cm or more, with a line broadening of only 100 hertz (*36*).

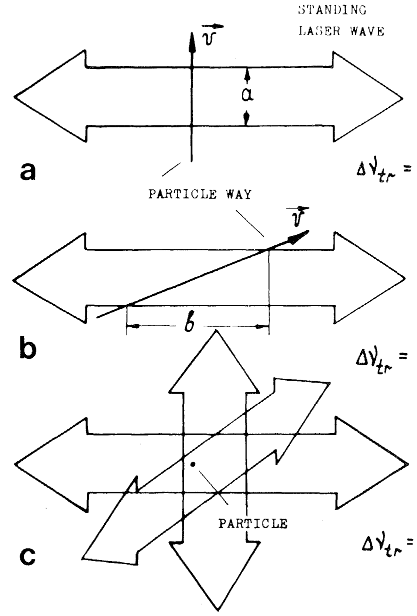


Fig. 8. Transit broadening of narrow resonance in various spectroscopic methods: (a) saturation spectroscopy, (b) two-photon spectroscopy, and (c) particle trapping in a three-dimensional potential field.

Trapped Particle Spectroscopy

Unlike the previous two approaches, trapped particle spectroscopy is still in the theoretical state. However, its potential merits are high. The idea of the method is that the Doppler shift of an absorption or emission line can be eliminated if the translational motion of a particle can be transformed into an oscillatory motion with amplitude *a* less than the radiation wavelength λ. This method is widely used in microwave spectroscopy and is known as the Dicke method (*37*). In the optical region it requires that the motion of a particle be restricted to a negligible volume $\sim \lambda^3$. Letokhov (*38*) suggested that a nonresonant strong standing light wave should be employed for this purpose. The wave might act as a potential space-periodic field, trapping particles with low velocities. A neutral particle (atom or molecule) in a high-frequency electromagnetic field is acted upon by a force proportional to the mean square gradient of the electric field intensity. Under this force the particles are pulled into the standing wave loops.

The depth of the potential dips in the standing wave loops will be $U_{\mathrm{m}} = 2\pi\alpha I/c$, where α is the polarizability of particles in a nonresonance field, I is the radiation intensity, and c is the speed of light. For an atom or molecule with a typical polarizability $\alpha = 3 \times 10^{-24}$ cm^3 in a standing wave of intensity $I = 10^3$ watt/cm^2, the depth of the potential dip will be $U_{\mathrm{m}} = 3.9 \times 10^{-12}$ electron volt. In such a potential field only particles with kinetic energy $^1/_2 Mv^2 < U_{\mathrm{m}}$ can be trapped—that is, particles whose velocity is 10^4 to 10^5 times less than the mean thermal velocity. For three-dimensional trapping we can employ a three-dimensional standing wave formed by crossing three mutually perpendicular standing waves (*39*). Where the three standing waves cross, particles whose velocities are less than a certain critical velocity, $v_{\mathrm{cr}} = (2U_{\mathrm{m}}/M)^{1/2}$, will make a finite motion in the elementary volume $(\lambda/2)^3$. For such particles Doppler broadening of spectral lines will disappear, and at the center of each spectral line there will be a narrow component with the natural width 2Γ. Application of the method is possible only if $\Gamma < kv_{\mathrm{cr}}$.

The main problem of the method is detecting the narrow resonances, since only an extremely small fraction of the particles in a thermal distribution [approximately $(v_{\mathrm{cr}}/v_0)^3$, or 10^{-12} to 10^{-15}] participate in their formation. At a low gas pressure, which is needed to eliminate collisions and to obtain a small homogeneous width 2Γ, one particle or less will be trapped in a volume of 1 cm^3. This density is many orders of magnitude less than the density of trapped particles in the case where one particle is located in each elementary volume $(\lambda/2)^3$. The difficulty can be obviated if slow particles can be sorted and stored to a maximum density $N_{\max} \simeq (2/\lambda)^3$ in the volume occupied by a three-dimensional light wave.

In spite of the practical difficulties inherent in the method of particle trapping, it is worthy of attention because of its universal nonresonance nature. When there is a strong light field only at one frequency beyond the resonance frequencies of the particles, it is possible to attain narrow peaks at the center of the Doppler profiles for any particles. The restriction on resolving power imposed by the transit time of the particles through the light beam is eliminated (*39*). In the methods previously considered a resolving power of the order of 10^{10} to 10^{11} can be achieved only by using light beams tens of centimeters in diameter.

Narrowing of optical spectral lines by ion storage in an electric field was discussed recently (*40*). The physics involved in eliminating the Doppler broadening in this case is the same as in neutral particle trapping in a standing light wave, although the trapping mechanisms differ materially.

Comparison of Resolving Power in the Three Methods

In absorption saturation spectroscopy the "instrumental width" of spectral lines is determined mainly by two effects: (i) transit broadening, due to the transit time of particles interacting with the field (Fig. 8a), which is given by $\Delta\omega_{tr} \simeq v_0/a$, where v is the mean thermal velocity of particles and a is the diameter of the light beam, and (ii) geometrical broadening, caused by distortion of the wave front and given by $\Delta\omega_{geom} \simeq \Delta\omega_{tr}\delta l/\lambda$, where δl is the maximum deflection of the surface of the wave front from a plane. In experiments by Hall and Borde (*41*) a beam 5 cm in diameter, with a plane wave front accurate within fractions of a wavelength, was used to obtain narrow resonances of CH_4 at the vibrational-rotational transition $F_1{}^2P(7)\nu_3$ ($\lambda = 3.39$ μm); their lines were about 10 khz in width, corresponding to a resolving power of 10^{10}. These two effects restrict the resolving power in saturation spectroscopy to about 10^{10} to 10^{11}—that is, before resonance broadening due to the second-order Doppler effect is taken into account. Naturally, it is essential that in any method the line width of the laser used to detect a narrow resonance inside the Doppler profile should be less than the width of the narrow resonance. This calls for lasers with very good frequency stability, since frequency instability is responsible for broadening the spectrum of the laser radiation.

In two-photon spectroscopy there is no geometrical broadening, and transit broadening can be reduced by ensuring that the particles move along the standing light wave rather than across it, as shown in Fig. 8b (*36*). It is possible to operate with interaction lengths of about 1 to 2 m, in which case $\Delta\nu_{tr} \ll 1$ khz. The main limitation on the resolution obtained in this method is due to the second-order Doppler effect, that is, the dependence of the central frequency of a line on the absolute velocity of the particle. The thermal distribution of absolute velocities of particles inevitably results in a second-order Doppler resonance broadening of $\Delta\nu'_{\mathrm{Dopp}} \simeq \nu_0 kT/Mc^2 \simeq \nu_0(v_0/c)^2$, where T is the gas temperature, M is the mass of a particle, and c is the speed of light; this limits the resolution obtained by this method at the level of $(c/v_0)^2$.

Table 4. Effects limiting the resolving power in nonlinear laser spectroscopic methods.

Method	Effect				
	Transit broadening	Geometric broadening	Second-order Doppler	Spectral width of laser radiation	Instrumental limit of resolving power
Saturation spectroscopy	Yes	Yes	Yes	Yes	10^{10}–10^{11}
Two-photon spectroscopy	Reduced	No	Yes	Yes	10^{12}–10^{13}
Trapped particle spectroscopy	No	No	No	Yes	10^{13}–10^{15}

In particle trapping all these limitations, except the effect of laser line width, disappear. The instrumental restrictions on the resolving power for all three methods of nonlinear laser spectroscopy are compared in Table 4.

Comparison of Sensitivity in the Three Methods

In general, the sensitivity of any method for detecting narrow resonances can be determined by measuring the maximum energy that can be absorbed by particles from the light wave at the 1—2 transition. The particles responsible for the formation of a narrow nonlinear resonance peak of homogeneous half-width Γ can not make stimulated transitions between levels 1 and 2 with a rate greater than Γ. Hence, the maximum power absorbed per unit volume is equal to

$$P_{\mathrm{abs}} < \hbar\omega_{12}\Gamma N_{\mathrm{int}}$$

where N_{int} is the density of particles in resonance with the light wave.

In absorption saturation the field is in resonance with a small fraction of the particles (those with a particular projection of their velocity), and the density of interacting particles is $N_{\mathrm{int}} \simeq (\Gamma/\Delta\omega_{\mathrm{Dopp}} N_0$, where N_0 is the total density of particles at levels 1 and 2. Thus, the sensitivity of this method drops as the resonance narrows.

In two-photon spectroscopy the standing light wave is in resonance with all particles, so that $N_{\mathrm{int}} = N_0$. This gives the method a material gain in sensitivity for observing very narrow resonances, which is of the order of $\Delta\omega_{\mathrm{Dopp}}/\Gamma \sim 10^3$ to 10^6. To attain a rate of induced two-quantum transitions of the order of Γ the standing light wave should have a much higher intensity than that used to induce one-quantum transitions, but this question is purely practical.

In the particle trapping method N_{int} is essentially equal to the number of trapped particles. In case of complete (three-di-

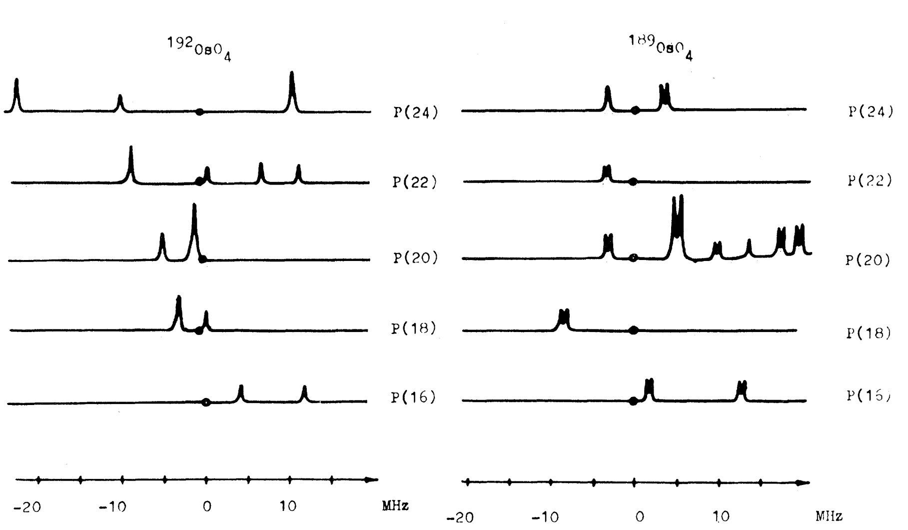


Fig. 9. Spectra of saturated absorption by $^{192}OsO_4$ and $^{189}OsO_4$ molecules measured through some *P* branch lines of a CO_2 laser at 10.6 μm (small circles denote the centers of CO_2 laser frequencies).

Table 5. Effects in atomic spectra.

Effect	Resolving power
Fine structure of excited levels	10^5 to 10^7
Isotopic structure	10^5 to 10^7
Hyperfine structure, including atoms with isomeric nuclei	10^5 to 10^8
Relativistic effects (Lamb shift)	10^6 to 10^8
Radiative broadening	10^6 to 10^9
Collisional broadening (at 1 torr)	10^7 to 10^9

mensional) particle capture, where the particles are trapped in a volume $(\lambda/2)^3$, the sensitivity drops proportionally to $(kv_{cr}/\Delta\omega_{Dopp})^3$.

To obtain narrow resonances by any of the three methods we have been discussing, it is necessary to reduce particle collisions so that the collisional broadening, $2\Gamma_{coll}$, is less than the resonance width, 2Γ. This can be done by reducing the pressure below 10^{-3} torr, which also decreases N_{int} and reduces the sensitivity attained.

Finally, the sensitivity of any method in nonlinear spectroscopy depends substantially on the method used to detect the energy absorbed by the gas. The change in intensity of the wave used to detect narrow resonances is usually measured after the wave passes through the gas cell. At very small absorptions this change is negligible, and the sensitivity is limited by the shot noise (fluctuations) of the detector. It is therefore much more useful to directly detect the value of the absorbed intensity. If the excited particles fluoresce, this can be done by recording the variation in the fluorescence intensity (*30, 31*). In this case the primary radiation does not enter the detector, and the sensitivity for detecting narrow resonances increases sharply. For example, narrow resonances in the fluorescence of CO_2, as the absorption is saturated by CO_2-laser radiation, have been detected at very low pressures of the gas (down to 10^{-5} torr) (*42*). This method would be equally appropriate for two-photon and trapped particle spectroscopy. Other methods of directly detecting excited particle concentrations, for example in induced absorption or atomic beams, are worth investigating. These possibilities have not been realized yet, but they promise a considerable increase in the sensitivity of nonlinear methods for experiments with very low atomic and molecular densities.

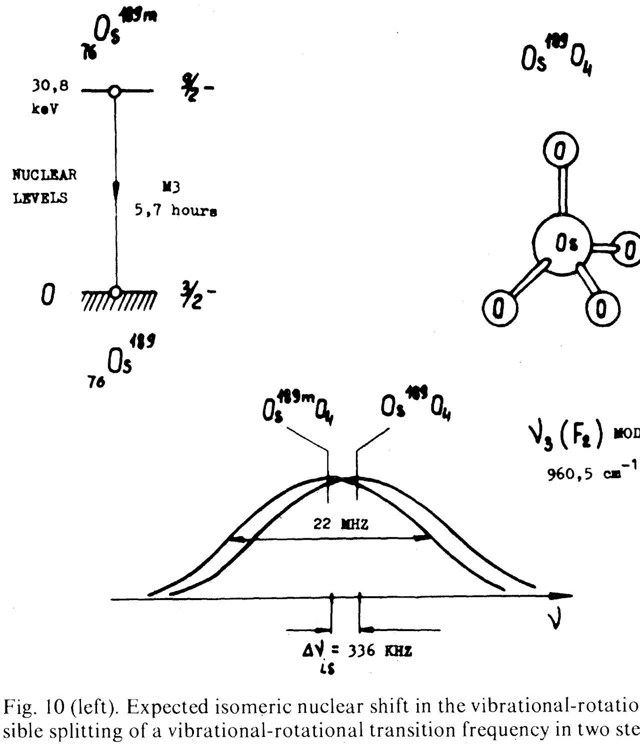
Spectroscopic Data

Experiments in which a resolving power of 10^8 is achieved are not uncommon at present. In the best experiments, using absorption saturation, a value of about 10^{10} has been attained (*41*)—that is, 10^5 times better than with the best classical spectrometers and 10^4 times better than with linear laser ones. In comparing the nonlinear laser methods I have stated that a resolving power of the order of 10^{13} to 10^{15} can be expected. This is determined by a fundamental limit, the natural width of the spectral lines of laser radiation. With these powerful nonlinear methods, what new spectroscopic information becomes available?

In Table 5 I list some effects in atomic spectra that can only be measured by methods in which Doppler broadening has been eliminated. A multiplet or fine structure is usually well resolved by classical methods, but for highly excited states the fine splitting decreases in proportion to n^3 (n is the principal quantum number) and is masked by the Doppler effect. To study isotopic and hyperfine structures, which depend on the spin and quadrupole moment of the nucleus, as well as the hyperfine structure of isomeric nuclei the resolving power has to be in the range 10^5 to 10^8. Many components of isotopic and hyperfine structure can be resolved by classical devices with high resolution (such as the Fabry-Perot interferometer) but it is necessary to work into the Doppler profile to investigate the structure fully. Before nonlinear laser spectroscopy was discovered it was possible to do this by narrowing spectral lines in an atomic beam or by microwave spectroscopy of the ground state and

Table 6. Effects in molecular spectra in the infrared.

Effect	Resolving power
Hyperfine structure due to quadrupole interaction	10^6 to 10^8
Collisional broadening (at 1 torr)	10^7 to 10^8
Hyperfine magnetic structure	10^9 to 10^{11}
Isomeric shift due to nuclear excitation	10^8 to 10^{10}
Difference of energy levels of left-hand and right-hand molecules due to weak interactions	10^{14} to 10^{15}



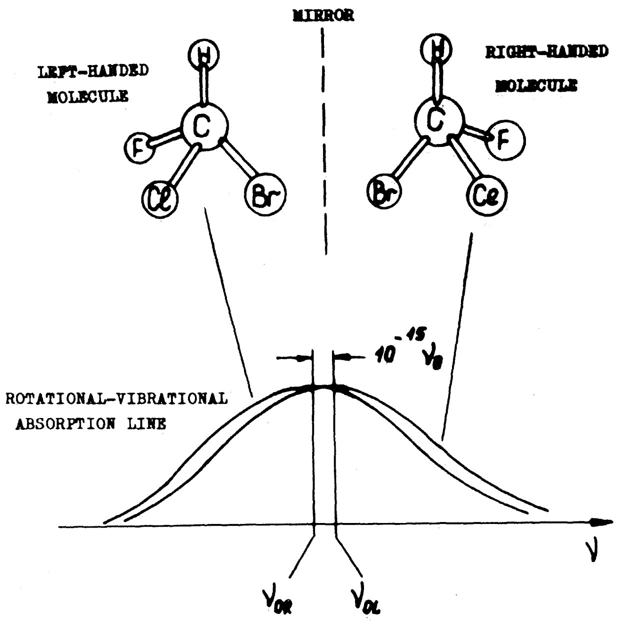


Fig. 10 (left). Expected isomeric nuclear shift in the vibrational-rotational transition of the $\nu_3(F_2)$ band of $^{189}OsO_4$ at 960.5 cm^{-1}. Fig. 11 (right). Possible splitting of a vibrational-rotational transition frequency in two stereoisomeric forms of a simple molecule. The splitting is caused by parity violation due to weak interactions between elementary particles in the molecule.

some excited states. For example, before nonlinear laser methods an atomic beam was needed in order to detect the hyperfine structure of the sodium *D* lines; now, with absorption saturation spectroscopy, such experiments can be done easily with a low-pressure gas (*43*). A classical example is the Lamb shift, which for level 2*S* of the hydrogen atom is smaller than the Doppler width of the H_α line; it has been detected in atomic excited states by microwave spectroscopy with an atomic beam, but now such measurements are made by the absorption saturation method (*44*) and they can be applied to atoms and ions in many energy states. Nonlinear methods also make it possible to measure spectral line broadening inside the Doppler contour caused by radiative decay and collisions.

In molecular spectroscopy, particularly in the infrared, classical methods do not provide very good resolution. Only with the advent of lasers was it possible to obtain infrared spectra of molecules with a resolving power better than 10^5. Table 6 is a list of effects in molecular spectra that must be measured by methods without Doppler broadening. The hyperfine structure of vibrational-rotational transitions depends on quadrupole and magnetic interactions. The quadrupole interaction gives rise to a splitting of vibrational-rotational lines by 10^6 to 10^7 hertz, depending on the quadrupole interaction constant and the molecular angular momentum. The first measurements of the quadrupole hyperfine structure of a molecule in the infrared were made on $^{12}CH_3{}^{35}Cl$ by Meyer *et al.* (*45*). Experiments on $^{189}OsO_4$ have also shown a quadrupole structure (*46*). Figure 9 shows lines of the ν_3 band in the nonlinear absorption spectrum of $^{189}OsO_4$ and $^{192}OsO_4$. The doublet structure is due to the quadrupole moment of the ^{189}Os odd nucleus. Analogous spectra of $^{187}OsO_4$, $^{190}OsO_4$, and $^{192}OsO_4$ show no such splitting because these Os nuclei have no quadrupole moment.

Magnetic interaction between the molecular angular momentum and the nuclear spin causes a much finer splitting ranging from 10^3 to 10^5 hertz. To detect this the resolving power must be about 10^9 to 10^{11} Hall and Borde (*41*) first successfully detected the magnetic hyperfine structure in a vibrational-rotational spectrum in experiments with $^{12}CH_4$; their resolving power was about 10^{10}.

Nuclear excitation in a molecule affects the molecular vibrational frequencies since the nuclear excitation energy is equivalent to a decrease in the nuclear mass by $\Delta m = \Delta E_{\text{nuc}}/c^2$ (isomeric shift) (*47*). An expected isomeric shift in the vibrational spectrum of $^{189}OsO_4$ is shown in Fig. 10. The shift of the ν_3 vibration frequency of OsO_4, caused by an increase in the internal energy of the Os nuclei, would range from 0.3 to 2.0 Mhz for nuclear energies from 30 to 170 kev in various Os isomers (*46*). Using this effect it may be possible to measure the energies of metastable nuclei with high accuracy, whatever type of radioactive decay they undergo, by infrared molecular spectroscopy.

There is another very fine effect in molecular spectra which lies beyond the scope of present experiments but in future may be detected by methods of nonlinear laser spectroscopy. Two molecules that are mirror images of each other have different energy levels because of parity violation due to weak interactions between the electrons and nucleons in a molecule (Fig. 11) (*48*). Physically, the effect occurs when the energy of the system contains a small admixture of odd potential of interaction between the electrons and nucleons. Thus, for example, the vibrational energies of left- and right-handed molecules become different by an extremely small amount, of the order of 10^{-15} electron volt. If this effect were detected it might be possible to gain some insight into the fact that all natural proteins are composed of L-amino acids (the left-handed isomeric form). This effect in biology was discovered by Pasteur more than a century ago, but has not yet been fully explained.

Conclusion

Nonlinear, high resolution laser spectroscopy is a very effective tool for studying the structure of matter at the atomic and molecular level. This short review of the latest ideas and achievements in the field testifies to its rapid progress. Many advanced methods are being introduced into laboratory practice. Developments in tunable infrared and visible lasers indicate that commercial nonlinear laser spectrometers will be available in the near future.

New methods of nonlinear spectroscopy without Doppler broadening are being studied, with the ultimate goal of achieving a resolving power of 10^{14} to 10^{15}, where the limit will be set by the natural width of the laser line. When this is reached, nonlinear laser spectroscopy, like any really new research method, will find many far-reaching applications. I mentioned above its potential applications in nuclear spectroscopy and biology. Some of the applications in nuclear spectroscopy, which are so far only theoretical (*49, 50*), should be supported by experimental results within the next few years.

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