CHAPTER 1

BASIC CONCEPTS OF NONLINEAR SPECTROSCOPY AND RESONANT NONLINEAR OPTICS FOR TRANSITIONS BETWEEN DISCRETE LEVELS

The methods of high- and ultrahigh-resolution nonlinear laser spectroscopy is the investigation of the shapes of the narrow nonlinear resonances that appear on the Doppler contour of a spectral gain or absorption line of a weak probing (or spontaneous-emission) field acted upon by strong quasimonochromatic laser radiation. The theory of nonlinear optical processes in which transitions to the continuous spectrum participate, while having a number of specific features, is a development and generalization of the corresponding results for the discrete spectrum. We consider therefore briefly the basic premises of nonlinear spectroscopy and of resonant nonlinear optics for transitions solely between discrete levels.

1. Classification of Nonlinear Effects in Spontaneous-Emission, Amplification, and Absorption Spectra in Three-Level Quantum Systems

The investigation of interactions between two radiation fields and three-level quantum systems played an important role in laying the foundations of nonlinear spectroscopy. This question is elucidated in sufficient detail in a number of reviews and monographs (see, e.g., [1, 2]). In the usual formulation of the problem of resonant interaction between two radiation fields and a three-level quantum system one radiation is perturbing ("strong") while the other is probing ("weak"). In this formulation of the problem the absorption (gain) of the probing radiation on an adjacent transition plays the role of an observation process that determines the changes introduced by the field into the quantum system. It is precisely this case, by virtue of its simplicity, that was investigated in most theoretical and experimental studies.

The usual classification of radiative processes (spontaneous emission, scattering, two-photon absorption, etc., see, e.g., [3]) is based on perturbation theory, i.e., the energy of the interaction between the atom and the electromagnetic field is assumed low. It is in this approach that the notions of stepwise and two-photon transitions, of virtual states, etc., arise. This classification is connected with the existence of certain correlation properties, whereby the emitted photon "remembers" the absorbed one. Thus, the demarcation between stepwise and multiphoton processes is based in essence on their frequency–correlation properties. The notion of the stepwise and two-photon processes was developed in [4]. It was shown that if the energy of the interaction between the atom and the field is on the order of or larger than the level width, an if perturbation theory in its usual variant is not applicable, then the aforementioned fundamental concepts must be altered. It turns out that with increasing field (or with decreasing deviation of the strong field from resonance) the frequency–correlation properties of radiative processes undergo substantial changes. As a result, certain differences between stepwise and two-photon processes decrease with increasing field intensity, and in sufficiently strong fields these processes become utterly indistinguishable. As a result, the manifestation of Doppler broadening is also substantially changed in strong fields. The ensuing phenomena can be tracked in the emission spectra. The subdivision of radiative processes into stepwise and multiphoton ones has thus little meaning in strong resonant fields.

In such cases it is convenient to classify the influence of a strong resonant field on the emission spectrum of a weak one as consisting of three effects [5]. Each of them can in principle, under certain conditions, manifest itself independently of the others. If the levels with which the strong radiation interacts are not populated or have equal populations, the change of the line shape of the adjacent transition is due only to the splitting effect. The first effect manifests itself in a deformation or splitting of the line contour on the adjacent transition; this is interpreted as the appearance of two quasilevels in the strong field. It turns out that in this case those adjacent-transition characteristics which are not integral with respect to frequency remain unchanged.

The second (population-dependent) effect is connected with the redistribution of the level populations under the influence of the strong radiation. The adjacent-transition characteristics that are integral with respect to frequency are altered only by this effect.

The third effect constitutes interference between processes that proceed via different sublevels. It manifests itself in the fact that the absorption or emission probability depends not only on the level populations but also on the polarization of the medium, induced by the transition that is resonant to the strong field. This nonlinear interference effect likewise leaves the integral absorption (the gain on the adjacent transition) unchanged, but may cause even reversal of the sign of the gain (absorption) as a function of the probing-radiation frequency. With increasing deviation of the strong radiation from resonance and with decrease of its intensity, the conjunction of the indicated phenomena can be interpreted on the basis of the concepts of stepwise and two-photon processes.

Nonlinear processes manifest themselves in gases usually under conditions of Doppler broadening of the transitions on account of the thermal motion of the atoms. Monochromatic radiation of not too high intensity and resonant within the confines of the Doppler emission line interacts in this case only with those atoms whose deviation from resonance is offset by the Doppler shift. In this case resonant nonlinear processes take the form of abrupt nonlinear structures on the Doppler emission or absorption contour of the probing field [1-8]. Let us consider the expressions that describe the phenomena listed above.

2. Emission and Absorption of Radiation on Discrete Transitions in the Presence of a Strong Field on an Adjacent Transition

2.1. General Expressions for the Probing-Field Emission and Absorption Power in the Presence of a Strong Field. Consider the photon emission of two monochromatic fields that interact with an atom whose term system is shown in Fig. 1.1. One of the fields with amplitude E is assumed strong and at resonance with the transition m–n; the corresponding matrix element in the case of a traveling wave is

$$\hbar^{-1}V_{mn}\exp\{i\omega_{mn}t\} = G^*\exp\{-i(\Omega t-\mathbf{kr})\}, \tag{1.1}$$

where $G = -\mathbf{d}_{mn}\mathbf{E}/2\hbar$; $\Omega = \omega - \omega_{mn}$; ω and $\mathbf{k}$ are the frequency and wave vector of the radiation; ω_{mn} and $\mathbf{d}_{mn}$ are the frequency and matrix element of the electric dipole moment of the mn transition.

We shall be interested in emission (or absorption) of photons of the "weak" interaction, which is at resonance with one of the four transitions n → j, m → l, f → m, g → n (see Fig. 1.1). We consider first the case n → j. The weak field with amplitude E_μ will also be regarded as a traveling plane wave

$$\hbar^{-1}V_{nj}\exp\{i\omega_{nj}t\} = G_\mu^*\exp\{-i(\Omega_\mu t-\mathbf{k}_\mu\mathbf{r})\},\quad G_\mu = -\mathbf{d}_{jn}\mathbf{E}/2\hbar,\quad \Omega_\mu = \omega_\mu - \omega_{nj}. \tag{1.2}$$

It follows directly from the equations below for the diagonal elements of the density matrix that the power of the absorption or of the stimulated emission by a single atom or in a unit volume (depending on the normalization of the density matrix) is given by

$$w_{nj} = \hbar\omega_{nj}2\mathrm{Re}\,\langle iG_\mu^*\exp\{-i(\Omega_\mu t-\mathbf{k}_\mu\mathbf{r})\}\rho_{jn}\rangle, \tag{1.3}$$

where the angle brackets denote averaging over the atom velocities $\mathbf{v}$. In the situation described, stationary solutions are possible. We start out, therefore, from the equations for the density matrix average over the excitation moments of the atomic levels, assuming that the atoms move with velocity $\mathbf{v}$:

$$\begin{aligned}
&L_{jj}\rho_{jj} = \gamma_{nj}\rho_{nn} + q_j,\ L_{jj} = \partial/\partial t + \mathbf{v}\nabla + \Gamma_j,\\
&L_{jn}\rho_{jn} - i\hbar^{-1}V_{mn}e^{i\omega_{mn}t}\rho_{jm} = i\hbar^{-1}V_{nj}^*e^{-i\omega_{nj}t}(\rho_{nn}-\rho_{jj}),\\
&L_{jm}\rho_{jm} - i\hbar^{-1}V_{mn}^*e^{-i\omega_{mn}t}\rho_{jn} = -i\hbar^{-1}V_{nj}^*e^{-i\omega_{nj}t}\rho_{nm};
\end{aligned} \tag{1.4}$$

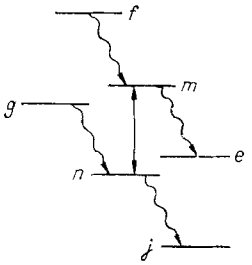

Fig. 1. Transition scheme for the investigation of resonant nonlinear processes in discrete spectra.

$$L_{mm}\rho_{mm} + 2\mathrm{Re}\,[i\hbar^{-1}V_{mn}e^{i\omega_{mn}t}\,\rho_{nm}] = q_m,$$
$$L_{nn}\rho_{nn} - 2\mathrm{Re}\,[i\hbar^{-1}V_{nm}e^{i\omega_{mn}t}\rho_{nm}] = q + \gamma_{mn}\rho_{mm}, \tag{1.5}$$
$$L_{nm}\rho_{nm} = i\hbar^{-1}V_{nm}e^{i\omega_{mn}t}(\rho_{nn} - \rho_{mm}),\quad L_{ik} = \partial/\partial t + \mathbf{v}\nabla + \Gamma_{ik}.$$

The equation systems are written in the "relaxation-constants" model, where Γ_{ik} is the transition width, $\Gamma_{ii} = \Gamma_i$; q_i denotes the rate of excitation of the level $i \equiv j$, m, n and does not depend on r and t. Equations (1.4) and (1.5) already take into acount the "weakness" of the field V_{jn}, i.e., it is assumed that the field hardly alters the populations. This is precisely why the complete system of equations for the density matrix turned out to consist of two systems: Eqs. (1.5) include only ρ_{mm}, ρ_{nm}, ρ_{nm} and the solution of this system is the starting point for the calculations of ρ_{jm}, ρ_{jn} from (1.4).

The solution of the system of equations entails no difficulty. The diagonal elements are independent of r and t, and the off-diagonal elements satisfy a simple exponential relation:

$$\rho_{ii} = r_i(\mathbf{v}),\quad i = m, n, j;$$
$$\rho_{nm}(\mathbf{r}, \mathbf{v}, t) = r_{nm}(\mathbf{v})\exp\{i(\Omega t - \mathbf{kr})\};$$
$$\rho_{jm}(\mathbf{r}, \mathbf{v}, t) = r_{jm}(\mathbf{v})\exp\{i[(\Omega_\mu + \Omega)t - (\mathbf{k}_\mu + \mathbf{k})\mathbf{r}]\}, \tag{1.6}$$
$$\rho_{jn}(\mathbf{r}, \mathbf{v}, t) = r_{jn}(\mathbf{v})\exp\{i\Omega_\mu - \mathbf{k}_\mu\mathbf{r}\}.$$

Substituting (1.6) in (1.4) and (1.5) and equating the coefficients of like exponentials, we obtain for r_i, r_{nm}, r_{jn}, r_{jm} a system of algebraic equations, whose solution is of the form

$$r_j = n_j + \frac{\gamma_{nj}}{\Gamma_j}r_n;\quad r_n = n_n + \frac{2\pi|G|^2}{\Gamma_n\sqrt{1+\varkappa}}\left(1 - \frac{\gamma_{nm}}{\Gamma_m}\right)(n_m - n_n)W_B(\mathbf{v}),$$

$$r_m = n_m - \frac{2\pi|G|^2}{\Gamma_m\sqrt{1+\varkappa}}(n_m - n_n)W_B(\mathbf{v});$$
$$r_{nm} = -\frac{iG(r_m - r_n)}{\Gamma + i\Omega'}, \tag{1.7}$$
$$r_{jn} = iG_\mu\frac{\left[\Gamma_{jm} + i(\Omega' + \Omega'_\mu)\right](r_n - r_j) + iG^*r_{nm}}{\left[\Gamma_{jn} + i\Omega'_\mu\right]\left[\Gamma_{jm} + i(\Omega'_\mu + \Omega')\right] + |G|^2}.$$

We have introduced in these expressions the notation

$$n_i = \frac{q_i(\mathbf{v})}{\Gamma_i} + \frac{\gamma_{ki}}{\Gamma_i}\cdot\frac{q_k(\mathbf{v})}{\Gamma_k};$$

$$W_B(\mathbf{v}) = \frac{\Gamma_B/\pi}{\Gamma_B^2 + (\Omega - \vec{\mathbf{k}}\mathbf{v})^2};\quad \Gamma_B = \Gamma\sqrt{1+\varkappa};\quad \Gamma = \Gamma_{nm}; \tag{1.8}$$

$$\varkappa = \tau^2|G|^2 = \frac{2(\Gamma_m + \Gamma_n - \gamma_{mn})|G|^2}{\Gamma\Gamma_m\Gamma_n};\quad \Omega' = \Omega - \mathbf{kv};\quad \Omega'_\mu = \Omega_\mu - \mathbf{k}_\mu\mathbf{v}.$$

The function $n_i(\mathbf{v})$ is the distribution of the atoms in velocity on the level i in the absence of a strong field (at G = 0); this distribution is determined by the excitation rate $q_i(\mathbf{v})$. We assume that $q_i(\mathbf{v})$ is at equilibrium:

$$q_i = Q_i W_M(\mathbf{v}),\ W_M(\mathbf{v}) = (\sqrt{\pi}\bar{v})^{-3} \exp\{-\mathbf{v}^2/\bar{v}^2\},$$
$$\bar{v}^2 = 2kT/m. \tag{1.9}$$

If W(**v**) is regarded as a δ function, we have a one-velocity beam. With the aid of (1.2), (1.6), and (1.7) we obtain the following expression for the emission (absorption) power:

$$w_{nj} = 2\hbar\omega_{nj} |G_\mu|^2 \operatorname{Re}\left\langle \frac{\left[\Gamma_{jm} + i\left(\Omega'_\mu + \Omega'\right)\right](r_n - r_j) + ir_{nm}G^*}{\left[\Gamma_{jm} + i\left(\Omega'_\mu + \Omega'\right)\right]\left[\Gamma_{jn} + i\Omega'_\mu\right] + |G|^2} \right\rangle. \tag{1.10}$$

We turn now to the other transitions in which the levels m and n perturbed by the external field can take part (see Fig. 1.1). The emission and absorption power is calculated in all these cases in accord with a single scheme, and we present only the calculation results:

$$w_{gn} = 2\hbar\omega_{gn} |G_\mu|^2 \operatorname{Re}\left\langle \frac{\left[\Gamma_{gm} + i\left(\Omega'_\mu - \Omega'\right)\right](r_g - r_n) + ir_{mn}G}{\left[\Gamma_{gn} + i\Omega'_\mu\right]\left[\Gamma_{gm} + i\left(\Omega'_\mu - \Omega'\right)\right] + |G|^2} \right\rangle, \quad r_g = n_g; \tag{1.11}$$

$$w_{ml} = 2\hbar\omega_{ml} |G_\mu|^2 \operatorname{Re}\left\langle \frac{\left[\Gamma_{nl} + i\left(\Omega'_\mu - \Omega'\right)\right](r_m - r_l) + ir_{mn}G}{\left[\Gamma_{ml} + i\Omega'_\mu\right]\left[\Gamma_{nl} + i\left(\Omega'_\mu - \Omega'\right)\right] + |G|^2} \right\rangle, \quad r_l = n_l + \frac{\gamma_{ml}}{\Gamma_l} r_m; \tag{1.12}$$

$$w_{fm} = 2\hbar\omega_{fm} |G_\mu|^2 \operatorname{Re}\left\langle \frac{\left[\Gamma_{nf} + i\left(\Omega'_\mu + \Omega'\right)\right](r_f - r_m) + ir_{nm}G^*}{\left[\Gamma_{mf} + i\Omega'_\mu\right]\left[\Gamma_{nf} + i\left(\Omega'_\mu + \Omega'\right)\right] + |G|^2} \right\rangle, \quad r_f = n_f. \tag{1.13}$$

Equations (1.11)-(1.13) are of the same type as (1.10) and can be replaced by simply interchanging the subscripts and the signs. For example, (1.12) is obtained by making the substitutions m ↔ n, j → l, Ω' → −Ω '.

Equations (1.10)-(1.13) enable us to analyze not only stimulated emission and absorption of the weak field, but also spontaneous emission. To this end it suffices to discard from the expressions for w_{ik} those terms that correspond to absorption, and introduce in lieu of $|G_\mu|^2$ a quantity corresponding to the interaction of the atoms with the zero-point oscillations of the field: $|G_\mu|^2 = \gamma_{ik}\Delta\Omega_\mu\Delta 0/8\pi^2$.

2.2. Classification of Strong-Field Effect. Equation (1.10) is a clear reflection of the classification of the effects of the external field.

1. The denominator is quadratic in Ω_μ and contains therefore resonances at two frequencies. This circumstance can be interpreted as splitting of the atomic levels in the external field.

2. The numerator in (1.10) contains two terms with substantially different properties. The first is proportional to the population level $r_n - r_j$, which has a nonequilibrium part due to the selectivity of the interaction of the atoms with the external field (Bennett "holes"). This selectivity is reflected in the factor $W_B(\mathbf{v})$, which we shall henceforth call the *Bennett distribution*.

3. The second term, proportional to r_{nm} and also due to the presence of the external field, makes in a certain sense an unusual contribution to the radiation at the transition n → j. It is easily seen that the integral of w_{nj} with respect to Ω_μ is determined only by $r_n - r_j$:

$$\int_{-\infty}^{\infty} w_{nj} d\Omega_\mu = 2\pi\hbar\omega_{nj} |G_\mu|^2 \langle r_n - r_j \rangle. \qquad (1.14)$$

Actually the two roots of the denominator of (1.10) lie in the upper complex-frequency half-plane. Choosing the integration contour along the real axis and an infinite semicircle in the lower half-plane we verify that the integral of the second term of (1.10) with respect to Ω_μ is identically zero. The term with r_{nm} alters therefore only the shape of the line but not its integrated intensity. The very presence of this term and its indicated property are in no way restricted to the particular problem considered. Indeed, it can be seen from (1.4) that, at any composition of the strong field, the "sources" that "excite" ρ_{jm}, ρ_{jn} are both the population difference $\rho_{nn} - \rho_{jj}$ of the combining levels and the off-diagonal element ρ_{nm} induced by the external field. Therefore w_{nj} will contain ρ_{nm} also in a general case, not only when the external field is monochromatic. It can be stated that this term reflects the "coherence" introduced into the state of the atom by the strong field, and as a result the weak field "intermixes" not only the states n and j, but also m and j. The latter leads to the onset of oscillations at the frequency $\omega + \omega_\mu$ (see ρ_{jm} in (1.6)). These properties of the term with r_{nm} allow us to refer to the effects that it produces as *nonlinear interference effects*.

Expression (1.10) can be regarded as the difference between the number of acts of emission and absorption of a photon $\hbar\omega_\mu$. If $r_j = 0$, only emission is possible in the system. Therefore all the terms in w_{nj} except r_j determine emission processes. On the contrary, whatever is connected with r_j specifies the rate of absorption of the weak-field energy.

If follows thus from (1.10) that the change of the absorption is due only to the splitting of the level, since the absorption corresponds to a transition from an unperturbed level j to a perturbed level n. The nonlinear interference effects are connected with the reverse transition from the perturbed state into the unperturbed, i.e., in the case of the $n \to j$ transition they are contained only in the emission.

The energies emitted and absorbed are, naturally, positive. The difference w_{nj} between them, however, can be either positive or negative. Moreover, the sign of w_{nj} can vary with the frequency Ω_μ. This is also an interference effect: it can be seen from (1.10) that the difference between the absorption and emission contours is due only to the term with r_{nm}, which can alter quite substantially the emission line shape.

The level-splitting effect is separated in pure form for a transition from an unperturbed level (j, g, f, ℓ) to a perturbed one (m, n). In the case $j \to n$ this corresponds to absorption. If n_m and n_n are small enough compared with n_j, we have

$$w_{nj} = -2\hbar\omega_{nj} |G_\mu|^2 \operatorname{Re} \left\langle \frac{r_j(v)}{\Gamma_{jn} + i\Omega'_\mu + |G|^2 [\Gamma_{jm} + i(\Omega'_\mu + \omega')]^{-1}} \right\rangle. \qquad (1.15)$$

The phenomena considered above can be analyzed also on the basis of the method of probability amplitudes, as is done, e.g., in [4]. The density-matrix method, however, is in our case more compact, universal, and lucid. Equations (1.10)-(1.13) allow us to investigate the shapes of the nonlinear resonances that appear on the spectral-line contour under the influence of a strong field and serve as the basis for the nonlinear-spectroscopy method. A more detailed treatment of this question is contained in [1-8].

3. Frequency Mixing in Resonant Nonlinear Media

The nonlinear processes considered above, such as multistep and multiphoton absorption and scattering, are not coherent, since their contribution to the polarization of the medium at the investigated frequency is determined by the squared modulus of the strong-field intensity. Among the processes that are coherent are those in which harmonics and combination frequencies are generated, since the source of the emission at these frequencies is the nonlinear polarization of the medium, proportional to the product of the intensities of the interacting fields. The frequency and phase of this polarization are determined by the sums of the frequencies and phases of the interacting waves. The most important condition for effective conversion of radiation on the basis of coherent processes is matching of the phases of the nonlinear polarization and of the radiation it emits.

The aggregate of the coherent and incoherent processes is the basis of the methods of nonlinear spectroscopy of matter, as well as of the methods of nonlinear optics, which help solve the most important problem of quantum electronics – the broadening of the frequency band of coherent radiation.

3.1. Distinguishing Features of Resonant Nonlinear Optics of Atomic-Molecular Media. Among the tasks of increasing the bandwidth of the generated radiation are, in particular, making coherent radiation feasible in the far UV and far IR bands, conversion of the weak-IR frequencies into more easily recorded frequencies, as well as conversion of cw and quasi-cw radiation in the case of strong irradiation of a nonlinear medium. A promising approach to the solution of these problems is the use of nonlinear processes in gaseous media. Among the advantages of this class of nonlinear media are transparency in a large spectral interval from the far infrared to the ultrasoft x-rays, high radiation endurance and self-recovery after breakdown, possibility of controlling the length of the wave phase matching by continuously varying the concentration and composition of the medium, as well as the possibility of ensuring large lengths and apertures of the nonlinear medium.

In view of the central symmetry, the free atoms have nonlinearites of odd order in the field amplitudes, starting with cubic. This favors management of the short-wave bands. Thus, in contrast to anisotropic crystals, gaseous systems have a higher order of nonlinearity and a lower concentration of active particles. This necessitates the use of relatively strong pumping to obtain high conversion coefficients. The last requirement, however, is possibly not so stringent, because resonant and quasiresonant nonlinear processes are used, since the nonlinear susceptibilities are strongly increased thereby. In addition, synchronism conditions can be controlled by tuning some of the frequencies of the interacting fields near resonance. Prerequisites are thus met for increasing the conversion coefficient and lowering the required pump intensities. Under resonance conditions, however, a much greater role is assumed by restrictive processes such as single- and multiphoton absorption and ionization, saturation, saturation and level-shift effects, nonmonochromaticity of the radiation, self-action of the radiation, and others. Thus, the prospects indicated require clarification and selection of the optimal conversion conditions such that the advantages of the resonant interactions are still in effect before the restrictive processes managed to evolve. All this calls for detailed investigation of the nonlinear processes in a nonresonant medium.

Substantial progress towards obtaining short-wave coherent vacuum ultraviolet and ultrasoft x rays was indeed made in recent years by using nonlinear processes of mixing frequencies of third, fifth, and seventh order in atomic-molecular media. The advantage of this approach is that it is based on the use of available visible and ultraviolet lasers, which require no cavities for short-wave radiation, and that the generated line width is determined by the corresponding pump-radiation characteristics. By retuning the pump radiation frequency it is possible to retune the lasing frequency in a sufficiently wide interval.

A survey of some of the progress in resonant nonlinear optics is contained in [9, 10]. We shall dwell briefly on the physical principle of radiation-frequency mixing in resonant gaseous media.

3.2. Conversion Coefficient. Consider frequency-mixing processes of the type $\omega_1 + \omega_2 + \omega_3 = \omega_s$. We represent the radiation fields and the polarization of the medium at each of the frequencies in the form

$$E_j(\mathbf{r}, t) = \frac{1}{2}\left[E_j(\mathbf{r})\, e^{i\omega_j t} + E_j^*(r)\, e^{i\omega_j t}\right],$$
$$\mathscr{P}_j(\mathbf{r}, t) = \frac{1}{2}\left[P_j(\mathbf{r})\, e^{-i\omega_j t} + P_j^*(r)\, e^{i\omega_j t}\right]. \tag{1.16}$$

Following [11-13], we assume each of the fields to be a TEM_{00} Gaussian mode focused at a point $z = f$ with confocal parameter b (f is the focal length of the lens):

$$E_j(\mathbf{r}) = E_{0j}(1 - i\xi)^{-1} \exp\{ik_j z - k_j(x^2 + y^2)/b(1 + i\xi)\}. \tag{1.17}$$

Here $k_j = 2\pi j/\lambda j = 2\pi_j \nu_j$; n_j is the refractive index at the frequency ω_j; $\nu_j = 1/\lambda_j$; λ_j the wavelength in vacuum; $b = 2\pi w_{0j}^2 \nu_j$; w_{0j} the cross-sectional radius of the light beam; and $\xi = 2(z - f)/b$. We assume all waves to be focused with the same confocal parameter.

Thus, at the points $z = f \pm b/2$ the area of the light spot is doubled compared with its area at the focus. Calculating the radiation intensity at the point (x, y) with the aid of (1.17) and integrating with respect to (x, y) we can obtain an expression for the total radiation power W_j in a Gaussian beam:

$$W_j = cE_{0j}^2 A_j/8\pi, \quad A_j = b\lambda_j/4. \tag{1.18}$$

A_j is the effective area of the Gaussian beam.

Assuming a radiation source having a frequency ω_S and a nonlinear polarization

$$P_S^{(3)}(\mathbf{r}) = N\langle\varkappa^{(3)}\rangle E_1(\mathbf{r}) E_2(\mathbf{r}) E_3(\mathbf{r})/4, \tag{1.19}$$

where $\omega_s = \omega_1 + \omega_2 + \omega_3$, and $\langle\varkappa^{(3)}\rangle$ is the atomic nonlinear susceptibility averaged over the atom velocities, we can obtain from Maxwell's equations in the approximation with given fields E_1, E_2, E_3, [11]

$$E_s(\mathbf{r}) = \frac{i\pi b k_s}{4} N\langle\varkappa^{(3)}\rangle E_{01}E_{02}E_{03} I(\Delta k, \xi, \zeta)(1+i\xi)^{-1}\exp\left\{ik_s z - \frac{k_s(x^2+y^2)}{b(1+i\xi)}\right\}. \tag{1.20}$$

In (1.19) and (1.20), N is the density of the atoms; $\zeta = 2f/b$; $\Delta k = k_S - k_1 - k_2 - k_3$; the integral $I(\Delta k, \xi, \zeta)$ reflects the degree of synchronization of the nonlinear polarization and of the radiation it emits under the focusing conditions

$$I(\Delta k, \xi, \zeta) = \int_{-\xi}^{\xi} d\xi' \frac{\exp[(1/2)ib\Delta k(\xi - \xi')]}{(1+i\xi')^2}; \tag{1.21}$$

$\langle\varkappa^{(3)}\rangle$ is the cubic nonlinear susceptibility of the atoms or molecules, averaged over their velocities and also over the spectrum of the pump if the latter is not monochromatic.

The spatial structure of the nonlinear polarization and the focusing integral, which follow from an analogous consideration of mixings of the type $\omega_S = \omega_1 + \omega_2 - \omega_3$ and $\omega_S = \omega_1 - \omega_2 - \omega_3$, are somewhat different in form [13]. With the aid of (1.18) and (1.20) we can find expressions for the conversion of radiation having a frequency ω_3, with respect to power η_p and the number of photons η_q, into radiation of frequency ω_S in the given-pump-fields approximation. This expression is consequently valid for not too high coefficients of conversion and absorption over the length of the medium,

$$\eta_p = \frac{W_s}{W_3} = \frac{\nu_s}{\nu_3}\eta_q = \nu_1\nu_2\nu_3\nu_s\left|\frac{16\pi^2}{c}\langle\varkappa^{(3)}\rangle N\right|^2 F_j W_1 W_2 = \nu_3\nu_s\left|\frac{4\pi}{c}\langle\varkappa^{(3)}\rangle Nb\right|^2 F_j \frac{W_1}{A_1}\frac{W_2}{A_2}. \tag{1.22}$$

Equation (1.22) is valid not only for frequency addition but also for frequency subtraction. Here F_j is a function determined by the degree of phase matching of the nonlinear polarization and of the generated radiation in Gaussian beams having identical confocal parameters, and depends on the type of the nonlinear process j.

3.3. Phase Matching, Nonlinear Susceptibility, and Optical Resonant-Conversion Conditions. The form of the function F_j was investigated in detail in [13]. In the general case, for a nonlinear medium of length L, this function depends on the location of the focal point relative to the center of the medium (f/L), on the ratio of the confocal parameter to the length of the medium (b/L), on the phase mismatch over the length b (Δkb), as well as on the type of the process (k''/k'). Here $k'' = k_1 + k_2 + k_3$, and $k' = k_1 + k_2 \pm k_3$, respectively, at j = 1 and 2; $\Delta k = k_S - k'$; $k_{1,2,3,s}$ are the lengths of the radiation wave vectors.

In certain limiting cases F_j can be expressed analytically. Thus, for all process j in a plane wave ($b \gg L$) we have

$$F = \left[\frac{2L}{b}\frac{\sin(\Delta kL/2)}{\Delta kL/2}\right]^2, \quad \Delta k_{\text{opt}}L = \begin{cases} -4L/b, & j = 1, \\ 0, & j = 2; \end{cases}$$
$$F = 16L^2/\pi^2 b \quad \text{at} \quad L = L_c = \pi/\Delta k.$$

In the other limiting case $k' = k''$ (which holds for j = 1, and corresponds at j = 2 to the case $k_3 \ll k_{1,2}$), and for strong focusing ($b \leqslant L$) at the center of the medium (f/L = 0.5) we have

$$F_1 = \begin{cases} (\pi b \Delta k)^2 \exp(b\Delta k), & \Delta k < 0, \\ 0, & \Delta k \geqslant 0, \end{cases} \quad k''/k' \approx 1,$$
$$F_{1\max} = (\pi/1.36)^2 \quad \text{at } b\Delta k = -2; \tag{1.23}$$
$$F_2 = \pi^2 \exp(-b|\Delta k|), \ \Delta k \geqslant 0, \ \Delta k < 0, \ k''/k' \approx 1.$$

In the general case the plot of F is a curve with a maximum. For processes with subtraction (j = 2) this maximum decreases with increasing ratio k''/k'. It is easiest to ensure synchronism in strong focusing (at small b), especially for the process with subtraction ν_3(j = 2), for in this case synchronism is obtained at any sign of Δk. Synchronism for addition processes is possible only at Δk < 0. It is important that the magnitude and sign of k can be controlled by using an additional synchronizing gas additive.

The maximum value of η is thus determined by the maximum values of the factors contained in (1.22). In the general cases these parameters are interdependent and cannot be chosen arbitrarily. Let us consider some of these dependences.

For a one-component medium in which phase matching is achieved by varying the density N, we must maximize not the function F_j but $\eta \sim N^2 F_j \sim G = G(\Delta kb)^2 F_j$. Consequently a maximum of η is reached only when Δkb satisfies conditions that differ somewhat from (1.23). Besides the synchronism condition, N is subject to restrictions that stem from the condition that the single-photon and multiphoton absorptions be small. The latter, with allowance for the pressure dependence of the transition widths, can depend nonlinearly on the pressure. The dependence of the transition widths on N leads also to a dependence of the limiting values of W_i on N.

The pump powers W_i cannot be arbitrary. Given b and N, the radiation intensity at the focus must be such as not to lead to multiphoton absorption over the length b. Another important restriction on W/A is imposed by saturation effects. A decrease in the level-population difference causes a decrease of the nonlinear susceptibility. In addition, saturation effects alter the synchronism conditions. If the pulses are substantially shorter or substantially longer than the population lifetimes, it is possible in principle to set beforehand the pump intensity so that synchronism takes place during the greater part of the pulse duration, with allowance for the change of the level population. It is much more difficult to compensate for the inhomogeneity of the change of the population over the beam cross section and along the focusing region. In a number of cases effective interaction is possible also in a strongly perturbed medium. It is preferable, however, to choose for effective conversion conditions wherein saturation is avoided. As already mentioned, these conditions are also pressure dependent via the transition widths.

An important parameter in (1.22) is the nonlinear susceptibility $\varkappa^{(3)}$. If all the frequencies and their sum are substantially less than the frequency of the transition to the continuum, and if the contribution of the latter can be neglected, the formula for $\varkappa^{(3)}$ can be easily obtained in third-order perturbation theory, under conditions of two-photon resonance with the transition ng, by using the density-matrix method and Eq. (1.19):

$$\varkappa^{(3)} = \hbar^{-3}(\omega_1 + \omega_2 - \omega_{ng} - (\mathbf{k}_1 + \mathbf{k}_2)\mathbf{v} + i\Gamma_{ng})^{-1} \sum_{\substack{m \\ j=1,2}} \frac{d_{gm} d_{mn}}{\omega_j - \omega_{mg}} \sum_l d_{nl} d_{lg} \left(\frac{1}{\omega_s - \omega_{lg}} + \frac{1}{\omega_3 + \omega_{lg}} \right). \tag{1.24}$$

Here d_{ik} is the projection of the matrix elements of the electric dipole moments of the transitions on the direction of the electric field vectors, and Γ_{ng} is the Lorentz half-width of the two-photon transition line.

Thus, in the quasiresonant case $\varkappa^{(3)}$ is proportional to the product of the matrix elements of the dipole moments of the transitions that take part in the conversion process. If only the lower level is populated, it is inversely proportional to the product of the single-photon, and three-photon detunings of the interacting fields relative to the corresponding transitions coupled to the lower populated level. As already mentioned, each of these resonances increases the nonlinear susceptibility and is simultaneously accompanied by competing limiting absorption and saturation processes. The most stringent restrictions are imposed by resonances with the strongest single-photon transitions. The three-photon resonance corresponds to resonance between the generated frequency and an allowed transition. The latter corresponds frequently to weak transitions with a small jump of the principal quantum number. In these cases, when the conversion scheme is chosen, it is necessary to seek media and transi-

tions such that the generated frequency is close to that of the aforementioned transitions. The least stringent requirements occur in two-photon resonance between the pump and a forbidden transition. Two-photon pumping is therefore used most frequently in nonlinear-optics experiments.

If the pump is monochromatic, at exact two-photon resonance the corresponding detuning in the denominator $\varkappa^{(3)}$ is replaced, after averaging over the atom velocities, by the two-photon transition width, the Doppler width $2k\bar{v}$ at low pressure and the impact width Γ wherever $\Gamma \geq 2k\bar{v}$. The conversion coefficient therefore turns out to be inversely proportional to the width of the forbidden (two-photon) transitions. This leads to one more pressure dependence of the conversion coefficient.

The pumps frequently used in experiments, however, have a spectral width larger than that of the transitions. It was shown [14, 15] that in those cases when the spectral width is determined by independent modes, the conversion coefficient is inversely proportional to the product of the spectral widths of the two-photon transition and emission of the pump, and is proportional to the product of the pump powers averaged over the spectrum. From this follows a possibility of broadening the forbidden transitions in experiments on resonant nonlinear conversion of the radiation even with fields having a spectral width larger than that of the transitions. Another important conclusion is that if the lasing-line narrowing entails a power loss, such a procedure is unsuitable from the point of view of obtaining high conversion coefficients. The reason is that η decreases quadratically and the lasing power cubically with decreasing pump power, and increases linearly with decreasing pump line width.

The frequencies of the generated vacuum-ultraviolet and soft x-rays correspond most frequently to single-photon transitions from the ground state into a photoionization or dissociation continuum, which exerts a substantial influence on the nonlinear processes. In a number of cases the absorption of radiation generated via transitions into the continuum imposes a substantial restriction on the admissible densities N and hence on the maximum admissible values of η. Ways of surmounting this difficulty will be considered in Chaps. 3 and 4. It will be shown that nonlinear transmission resonances on a transition from the ground state into the continuum, with simultaneous increase of the nonlinear susceptibility, can be induced with the aid of an additional optical or infrared electromagnetic field. If the generated radiation is resonant with an autoionizing level, the increase of the nonlinear susceptibility can be accompanied by narrowing of this resonance. It becomes simultaneously possible to measure the radiative widths of the autoionizing levels.

We shall consider radiative processes on transitions into the continuum and into autoionizing states.

LITERATURE CITED

1. V. S. Letokhov and V. P. Chebotaev, Principles of Nonlinear Laser Spectroscopy [in Russian], Nauka, Moscow (1975).
2. S. G. Rautian, G. I. Smirnov, and A. M. Shalagin, Nonlinear Resonances in the Spectra of Atoms and Molecules [in Russian], Nauka, Novosibirsk (1979).
3. W. Heitler, The Quantum Theory of Radiation, Oxford Univ. Press (1954).
4. T. Ya. Popova, A. K. Popov, S. G. Rautian, and A. A. Feoktistov, "Nonlinear resonant radiative transitions," Zh. Eksp. Teor. Fiz., 57, No. 2, 444-451 (1969).
5. T. Ya. Popova, A. K. Popov, S. G. Rautian, and R. I. Sokolovskii, "Nonlinear interference effects in emission, absorption, and generation spectra," Zh. Eksp. Teor. Fiz., 57, No. 3, 850-863 (1969).
6. M. S. Feld and A. Javan, "Laser-induced line-narrowing effects in coupled Doppler-broadened transitions," Phys. Rev., 177, No. 2, 540-562 (1969).
7. M. S. Feld, "Laser saturation spectroscopy in coupled Doppler-broadened systems; how to find a needle in a haystack," in: Fundamental and Applied Laser Physics: Proceedings of the Esfahan Symposium, August 29-September 5, 1971, M. S. Feld, A. Javan, and N. Kurnit (eds.), Wiley (1973), pp.369-420.
8. Th. Hänsch and P. Toschek, "Theory of a three-level gas laser amplifier," Z. Phys., 236, 213-244 (1970).
9. J. J. Wynne and P. P. Sorokin, "Tuning in atomic vapors," Laser Focus, 11, No. 4, 62-69 (1975).
10. A. K. Popov, "Resonant nonlinear optics of gaseous systems," Avtometriya, 1, 112-128 (1978).

11. R. B. Miles and S. E. Harris, "Optical third-harmonic generation in alkali metal vapors," IEEE J. Quantum Electron., QE-9, No. 4, 470-487 (1973).
12. J. F. Ward and G. H. C. New, "Optical third harmonic generation in gases by a focused beam," Phys. Rev., 185, No. 1, 57-72 (1969).
13. G. C. Bjorklund, "Effects of focusing of third-order nonlinear processes in isotropic media," IEEE J. Quantum Electron., QE-11, No. 6, 287-295 (1975).
14. S. A. Stappaerts, G. W. Bekkers, G. F. Young, and S. E. Harris, "The effect of line width on the efficiency of two-photon pumped frequency convertors," IEEE J. Quantum Electron., QE-12, No. 6, 330-333 (1976).
15. V. I. Anikin, S. A. Akhmanov, K. N. Drabovich, and A. N. Dubovik, "Investigation of two- and three-photon resonances in atoms in a strong nonmonochromatic field," Kvantovaya Elecktron. (Moscow), 3, No. 9, 2014-2022 (1976).