Recent advances in nonlinear optics*

Y. R. Shen

Department of Physics, University of California and Inorganic Materials Research Division, Lawrence Berkeley Laboratory, Berkeley, California 94720

We present here a survey on the progress of nonlinear optics in recent years. Emphasis is on physical ideas, basic principles, and important experimental results.

CONTENTS

I.	Introduction	1
II.	Calculations of Nonlinear Optical Susceptibilities	2
III.	Second-Order Nonlinear Optical Processes	4
IV.	Optical Mixing in Vapor	5
V.	Stimulated Raman Scattering	7
VI.	Self-Focusing of Light	10
VII.	Some Third-Order Nonlinear Optical Effects	13
VIII.	High-Resolution Nonlinear Optical Spectroscopy	16
IX.	Transient Coherent Optical Effects	18
X.	Nonlinear Optical Effects in Plasmas	20
XI.	Nonlinear Optical Effects in Optical Waveguides	23
XII.	Multiphoton Ionization and Optical Breakdown	24
XIII.	Conclusions	26
Acknowledgment		27
References		27
Conference Proceedings and Review Books		32

I. INTRODUCTION

The advent of lasers has opened up a new frontier in physics. Among the many new fields of quantum electronics, nonlinear optics is one of the most interesting and exciting. Ever since the discovery of optical second-harmonic generation by Franken *et al.* (1961), the field of nonlinear optics has never stopped blooming.

The development of nonlinear optics since 1961 can be arbitrarily divided into three periods. In the first period (1961–1965), new nonlinear optical effects were being discovered at a tremendously rapid rate. These include sum- and difference-frequency generation, harmonic generation, parametric amplification and oscillation, multiphoton absorption, self-focusing, stimulated scattering, etc. Their potential usefulness was immediately recognized. Nonlinear optics soon became a major branch in the ever expanding field of quantum electronics. In the second period (1965–1969), new nonlinear optical effects such as nonlinear spectroscopy, transient coherent phenomena, optical breakdown, etc., were still being discovered. However, the main research effort was in achieving a better understanding of the known nonlinear optical effects in various media and in constructing useful nonlinear optical devices. In the third period (1969–1975), the field of nonlinear optics has become more and more mature. While discovery of new effects has been rare, the studies of nonlinear optics have been rapidly expanded into a new domain with the help of tunable lasers and ultrashort pulsed lasers, and have been extended to a wide range of different media. Applications of nonlinear optics have become more and more sophisticated. A glance at the recent publications in the journals would suggest that the golden era of nonlinear optics may be reaching an end, but it is definitely not over yet.

Over the past years, the field of nonlinear optics has been reviewed constantly by researchers in the form of books (Akhmanov and Khokhlov, 1964; Bloembergen, 1965; Butcher, 1965; Baldwin, 1969; Zernike and Midwinter, 1973) or review articles.[1] Nevertheless, review papers which survey the state of art of the field are rare. In this article, I shall give a survey on the progress of nonlinear optics in recent years. Emphasis will be on the physical ideas, basic principles, and important experimental results. It is difficult for me to give a complete coverage or even a complete bibliography of the recent work in this broad field. I should therefore apologize in advance to those whose important contributions happen to be accidentally omitted or improperly treated in this article.

Before we venture into the discussion of recent development, let us first give a quick review on the fundamentals of nonlinear optics (see, for example, Bloembergen, 1965). As is well known, all optical phenomena are governed by the Maxwell equations or the resulting wave equations

$$\left[\nabla\times(\nabla\times)+\frac{1}{c^2}\frac{\partial^2}{\partial t^2}\right]\vec{E}(\vec{r},t)=-\frac{4\pi}{c^2}\frac{\partial^2}{\partial t^2}\vec{P}(\vec{r},t),$$
$$\nabla\cdot\vec{E}(\vec{r},t)=-4\pi\nabla\cdot\vec{P}(\vec{r},t), \tag{1.1}$$

where $\vec{P}$ is the generalized electric polarization which includes not only the electric dipole part but also all the multiple contributions (Landau and Lifshitz, 1960; Bloembergen, 1965). In the weak-field limit, $\vec{P}$ is linear in $\vec{E}$, but in general $\vec{P}=f(\vec{E})$ is a nonlinear function of $\vec{E}$. If $f(\vec{E})$ is known, then we can in principle solve Eq. (1.1) and fully describe the nonlinear optical phenomena. Unfortunately, this is often not the case. The theoretical difficulties of nonlinear optics lie mainly in the correct description of $f(\vec{E})$ and in the solution of Eq. (1.1). Various approximations are necessary to circumvent the difficulties.

In many cases, we deal with interaction of several monochromatic or quasimonochromatic field components. We can usually expand $\vec{E}$ and $\vec{P}$ into Fourier components

*AEC Contract No. W-7405-eng-48.

[1]See, for example, articles in *Quantum Optics*, Proceedings of the International School of Physics "Enrico Fermi," Course XLII, edited by R. J. Glauber (Academic, New York, 1969); *Handbook of Lasers*, edited by F. T. Arecchi and E. O. Schulz-Dubois (North-Holland, Amsterdam, 1972); *Progress in Optics*, edited by E. Wolf (North-Holland, Amsterdam, 1961); *Progress in Quantum Electronics*, edited by J. H. Sanders and S. Stenholm (Pergamon, New York, 1969); "Sov. Phys.—Usp.," etc.

$$\vec{E}(\vec{r},t)=\sum_i \vec{E}(\omega_i), \quad \vec{P}(\vec{r},t)=\sum_i \vec{P}(\omega_i) \tag{1.2}$$

where $\vec{E}(\omega_i)=\vec{\mathcal{E}}(\omega_i)\exp(i\vec{k}_i\cdot\vec{r}-i\omega t)+$ and the polarization $\vec{P}(\omega_i)$ can often be written as a power series of $\vec{E}(\omega_j)$:

$$\begin{aligned}\vec{P}(\omega_i)=&\vec{\chi}^{(1)}(\omega_i)\cdot\vec{E}(\omega_i)\\&+\sum_{j,k}\vec{\chi}^{(2)}(\omega_i=\omega_j+\omega_k):\vec{E}(\omega_j)\vec{E}(\omega_k)\\&+\sum_{j,k,l}\vec{\chi}^{(3)}(\omega_i=\omega_j+\omega_k+\omega_l):\vec{E}(\omega_j)\vec{E}(\omega_k)\vec{E}(\omega_l)\\&+\cdots .\end{aligned} \tag{1.3}$$

In Eq. (1.3), $\vec{\chi}^{(n)}$ are the susceptibility tensors of the nth order. Clearly, the importance of $\vec{\chi}^{(n)}$ to nonlinear optics is the same as the importance of $\vec{\chi}^{(1)}$ (or the linear dielectric constant or refractive index) to linear optics. Therefore, it is not surprising that there has always been concerted research effort in nonlinear optics dealing with $\vec{\chi}^{(n)}$. In general, $\vec{\chi}^{(n)}$ should also depend on the wave vectors $\vec{k}_i$ of the field components, but in the electric-dipole approximation, the dependence on $\vec{k}_i$ is neglected. In this paper, we shall always assume electric-dipole approximation unless specified. We should also note that in special cases, the series of Eq. (1.3) can be summed up into a more compact form. This happens, for example, in dealing with saturation phenomena.

In many other cases, it is more convenient to use $\vec{E}(\vec{r},t)$ and $\vec{P}(\vec{r},t)$ directly instead of their Fourier components. This is especially true when one deals with transient nonlinear optical phenomena. The transient response of $\vec{P}(\vec{r},t)$ to $\vec{E}(\vec{r},t)$ should in principle obey an equation of motion, but such an equation is generally too complicated to be useful or solvable. There are, however, a number of simple but interesting cases where a simple equation for $\vec{P}(\vec{r},t)$ can be written down, as we shall see later (Sec. IX).

In solving a nonlinear optical problem, one often starts by imposing reasonable approximations on the problem, depending on the physical situation. This is most important since otherwise a general solution would be quite impossible. In the theory of nonlinear optics, making good and reasonable approximations is probably the most difficult, but crucial, practice.

We shall now proceed to discuss various special topics listed in the outline.

II. CALCULATIONS OF NONLINEAR OPTICAL SUSCEPTIBILITIES

We have seen in Eqs. (1.1)–(1.3) that the nonlinear wave propagation is prescribed by the susceptibility tensors $\vec{\chi}^{(n)}$. It is therefore important for us to know $\vec{\chi}^{(n)}$ in order to predict the nonlinear optical effects in a medium or to design a nonlinear optical device. Presumably, one can always obtain $\vec{\chi}^{(n)}$ from measurements, but for many purposes such as evaluation of new nonlinear optical materials, one would like to be able to predict $\vec{\chi}^{(n)}$ for a given medium. In fact, it would be a great triumph for the theory of matter if one could successfully predict $\vec{\chi}^{(n)}$. We shall discuss in this section only the calculation of the electronic contribution to $\vec{\chi}^{(n)}$ for a crystal.

Using quantum-mechanical perturbation calculations, one can always derive a complete expression for $\vec{\chi}^{(n)}$ in terms of frequency denominators and transition matrix elements (see, for example, Bloembergen, 1965). Nevertheless, such an expression is often not very useful since the calculations of transition frequencies and matrix elements are difficult. One has to use simplifying models or approximations to calculate $\vec{\chi}^{(n)}$.

An important simplifying assumption often used is to replace the frequency denominators in the expression of $\vec{\chi}^{(n)}$ by an average one. Then, through the closure property of the eigenstates, the sum of the matrix elements can be expressed in terms of moments of the ground-state charge distribution (Robinson, 1967, 1968; Jha and Bloembergen, 1968). The problem therefore reduces to the finding of the ground-state electronic wave function (Jha and Bloembergen, 1968; Flytzanis and Ducuing, 1969; Ducuing and Flytzanis, 1971).

The more successful simplifying model for calculating $\vec{\chi}^{(n)}$ is probably the bond model. In the early 1930's, the linear polarizability of a molecule or the linear dielectric constant of a crystal was calculated by the model assuming the bond additivity rule (Denbigh, 1940). According to the rule, the induced polarization on a molecule (or crystal) is the vector sum of the induced polarizations on all the bonds between atoms. Obviously, the same rule can be used in the simplifying calculations of $\chi^{(n)}$. Knowing the crystal structure, we need only to calculate the nonlinear polarizabilities of the bonds. We can write

$$\vec{\chi}^{(n)}=\sum_i \vec{\beta}_i^{(n)}, \tag{2.1}$$

where $\vec{\beta}_i^{(n)}$ is the nth-order polarizability tensor of the ith bond and the summation is over all the bonds in a unit volume.

The calculations of bond polarizabilities have been made simpler with the recent development of the bond theory (see, for example, Phillips, 1969, 1973). Assume a zincblende crystal made of identical bonds. Then, using the Penn model (Penn, 1962), we obtain for each bond in the low-frequency limit ($\omega\to 0$)

$$4N(\alpha_{\parallel}+2\alpha_{\perp})/3=\hbar^2\Omega_p^2/4\pi\bar{E}_g^2, \tag{2.2}$$

where $\alpha_{\parallel}$ and $\alpha_{\perp}$ are the bond polarizabilities parallel and perpendicular to the cylindrically symmetric bond, respectively, Ω_p is the plasma frequency of the N valence electrons per unit volume, and $\bar{E}_g$ is the average energy gap of the solid. In terms of the molecular orbital theory (see, for example, Coulson, 1961), $\bar{E}_g$ should correspond to the energy difference between the bonding and the antibonding states of the valence electrons constituting the bond, and can be decomposed into a homopolar gap E_h and a heteropolar gap C according to (Phillips, 1968 a, b)

$$\bar{E}_g^2=E_h^2+C^2 . \tag{2.3}$$

In Fig. 1, we show the wave functions of the bonding and antibonding states. Clearly, in the bonding state, there is a bond charge cloud between the two atoms. For a heteropolar bond, there is also a charge transfer from the less electronegative atom to the more electronegative

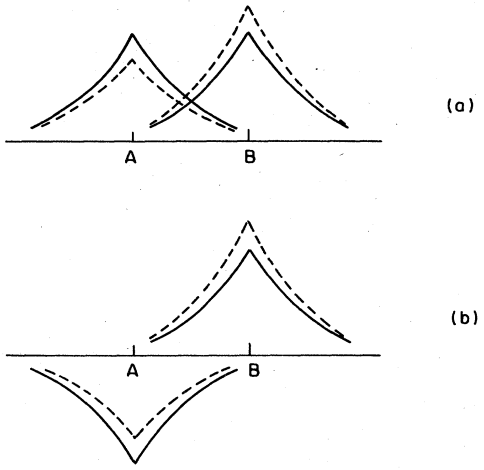

FIG. 1. Sketch of (a) bonding and (b) antibonding electron wave functions for an A–B molecule. Solid curves are for $A = B$ and dashed curves for $A \neq B$.

one. Such a charge distribution has also been verified by the empirical pseudopotential calculation (Walter and Cohen, 1971). The simple molecular theory shows that the charge transfer Q is related to the heteropolar gap C by

$$Q = -2eC/\bar{E}_g . \tag{2.4}$$

According to the bond theory of Phillips (1968c), we have

$$E_h^{-2} \cong ad^{2s}, \quad C \cong b(Z_A/r_A - Z_B/r_B)\exp(-k_s d/z) , \tag{2.5}$$

where a, b, and s are constant, Z_A and Z_B are the valences, r_A and r_B are the covalent radii of the A and B, atoms forming the bond, $d = r_A + r_B$ is the bond length, and $\exp(-k_s d/z)$ is the Thomas–Fermi screening factor. The bond charge is (Phillips, 1968 a,b)

$$q = -2e\bar{E}_g^2/(\bar{E}_g^2 + \hbar^2\Omega_p^2) , \tag{2.6}$$

which may be considered as a point charge sitting at a distance r_A and r_B away from the atoms A and B, respectively (Levine, 1969).

We now consider what happens when the bond is subject to an external field $\vec{E}$. The polarizabilities $\alpha_{\parallel}$ and $\alpha_{\perp}$ should of course be functions of $\vec{E}$ through the dependence of $\bar{E}_g$ on $\vec{E}$ in Eq. (2.2). We do not expect the bond length d to vary with $\vec{E}$. Hence, from Eq. (2.5), E_h should not depend on $\vec{E}$, except perhaps a higher-order correction. The field can, however, change the amount of charge transfer, or the position of the bond charge, or both. Consequently, according to Eqs. (2.4) and (2.5), C may depend strongly on $\vec{E}$. Then, in order to find $\vec{\beta}^{(n)}$, we only need to calculate the derivatives

$$\vec{\beta}^{(n)} = \partial^{(n-1)}\vec{\alpha}/(\partial\vec{E})^{(n-1)}$$
$$= [\partial^{(n-2)}/(\partial\vec{E})^{(n-2)}][(\partial\vec{\alpha}/\partial C)(\partial C/\partial\vec{E})] . \tag{2.7}$$

Two models have been used to calculate $\vec{\beta}^{(n)}$. The bond-charge model assumes that the field only affects the position of the bond charge (Levine, 1969; 1973 and references therein). Then the induced dipole moment on the bond is $\vec{p}(\vec{E}) = q\Delta\vec{r}$, and from Eq. (2.5), we have $\partial C/\partial\vec{E} = (\partial C/\partial\vec{r})\cdot(\partial\vec{r}/\partial\vec{E})$. The charge-transfer model assumes that the field only affects the amount of charge transfer (Tang and Flytzanis, 1971). The induced dipole moment on the bond is $\vec{p}(\vec{E}) = (\Delta Q)d$, and from Eq. (2.4) we have $\partial C/\partial\vec{E} = (\partial C/\partial Q)(\partial Q/\partial\vec{E})$.

Levine (1973), using the bond-charge model with some modification on Eq. (2.5), has calculated $\vec{\chi}^{(2)}$ and $\vec{\chi}^{(3)}$ for a large number of crystals of various kinds with apparent success. His calculated values are generally in very good agreement with the measured values. Tang and coworkers (Tang and Flytzanis, 1971; Tang, 1973; Scholl and Tang, 1973), on the other hand, have calculated $\vec{\chi}^{(2)}$ for a number of semiconductors using the charge-transfer model. Their results are also in good agreement with the measured values. Actually, both models are only crude approximations of the real situation. The empirical pseudopotential calculations (Walter and Cohen, 1971) indicate that the valence electrons in fact form a broad charge distribution around and along the bond, with its peak at the center of the bond. As examples, we show in Fig. 2 the charge distribution along a bond in Si and GaAs. In the presence of an external dc field, the charge distribution becomes slightly more asymmetric (qualitatively represented by the dashed curve in Fig. 2), but the peak of the distribution is not shifted (Louie and Cohen, 1975). Presumably, the field-induced shift of the position of the bond charge in the bond-charge model actually refers to the shift of the center of gravity of the valence charge distribution, while the field-induced charge transfer in the charge-transfer model refers to the slight change in the valence charge distribution around and along the bond, rather than net charge transferred from one ion core to the other.

In nonlinear optics, we are usually interested in materials with high nonlinearity. From what we have discussed, we should find materials with large nonlinearity in the bond polarizabilities. For large $\vec{\chi}^{(2)}$, we should in addition require that in summing $\vec{\beta}^{(2)}$ over all bonds [Eq. (2.1)] the vectorial cancellation is as small as possible. This means that the crystal structure should be as asymmetric as possible.

As we mentioned earlier, the above calculations are only good in the low-frequency limit. They are not valid when the optical frequencies are close or within the band absorption region since then the approximation of an average energy gap no longer holds. Those transitions

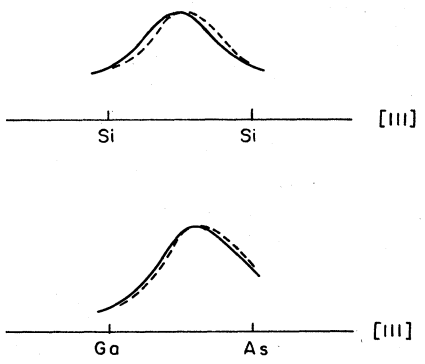

FIG. 2. Sketch of the charge distribution along a bond in (a) Si and (b) GaAs. Solid and dashed curves refer to cases with and without an external field, respectively.

with transition frequencies closer to the optical frequencies contribute more to $\vec{\chi}^{(n)}$. In order to calculate $\vec{\chi}^{(n)}$ in these cases, especially the dispersion of $\vec{\chi}^{(n)}$, one must use the full microscopic expression of $\vec{\chi}^{(n)}$. Such calculations with the assumption of constant matrix elements and certain approximate optical densities of states have been reported (Chang *et al.*, 1965; Bloembergen *et al.*, 1966; Parsons *et al.*, 1971; Bell, 1972). Recently, more rigorous calculations using the empirical pseudopotential method have been performed on some semiconductors (Fong and Shen, 1975). The results show that it is important to include the correct matrix elements and densities of states in the calculations.

III. SECOND-ORDER NONLINEAR OPTICAL PROCESSES

Second-order nonlinear optical effects are probably the most important and well-understood nonlinear optical phenomena. They are the basis for most of the existing nonlinear optical devices. The theory of these effects has long been worked out (see, for example, Bloembergen, 1965; Armstrong *et al.*, 1962). Here, we shall review briefly only the basic ideas in the theory.

For these nonlinear processes, we can reasonably assume the presence of only three quasimonochromatic fields.

$$\vec{E} = \vec{E}(\omega_1) + \vec{E}(\omega_2) + \vec{E}(\omega_3) \tag{3.1}$$

with $\omega_1 = |\omega_2 \pm \omega_3|$. In sum- and difference-frequency generation, $\vec{E}(\omega_2)$ and $\vec{E}(\omega_3)$ are the pump fields, while in parametric amplification, $\vec{E}(\omega_1)$ is the pump field. We can decompose Eq. (1.1) into three sets of equations, one for each $\vec{E}(\omega_i)$. These equations are nonlinearly coupled with one another through the polarizations

$$\vec{P}(\omega_1) = \vec{\chi}^{(1)}(\omega_1)\cdot\vec{E}(\omega_1) + \vec{\chi}^{(2)}(\omega_1 = |\omega_2 \pm \omega_3|):\vec{E}(\omega_2)\vec{E}(\omega_3), \text{ etc.} \tag{3.2}$$

The solutions of the coupled wave equations with the proper boundary conditions then fully describe the second-order nonlinear processes. They have already been obtained for a number of cases with appropriate approximations. These include the cases of sum- and difference-frequency generation with plane waves (Armstrong *et al.*, 1962), parametric amplification and oscillation with negligible depletion of pump power (Smith, 1972 and references therein), second-harmonic generation with focused beam (Boyd and Kleinman, 1968; Boyd *et al.*, 1965; Kleinman *et al.*, 1966; Bjorkholm, 1966; Kleinman, 1972), etc.

In recent years, the progress in this area has been mainly in finding new nonlinear crystals and in useful applications. The nonlinear crystals which receive much attention (see, for example, Singh, 1971; Kurtz, 1972) are the III–V compounds (GaAs, InSb, etc.), the II–VI compounds (ZnS, CdSe, etc.), the I–III–VI ($AgGaS_2$, $CuInS_2$, etc.) and II–IV–V ($CdSiAs_2$, $ZnGeP_2$, etc.) compounds, the KDP isomorphs (KH_2PO_4, RbH_2AsO_4, etc.), the ferroelectrics ($LiNbO_3$, $Ba_2NaNb_5O_{15}$, $LiIO_3$, etc.), the highly anisotropic crystals (Se, Te, HgS, etc.), and TGS, proustite, etc. These crystals have been noticed for their large $\vec{\chi}^{(2)}$. Depending on their regions of transparency, some are more useful in the visible and others in the infrared.

In most applications of second-order nonlinear optical effects, it is important to achieve phase matching

$$\Delta\vec{k} = \vec{k}_1 - \vec{k}_2 - \vec{k}_3 = 0,$$

where $\vec{k}_i$ is the wave vector of $\vec{E}(\omega_i)$. The energy conversion between the pump field (or fields) and the signal field will then be efficient. For a large interaction length, one would like to use collinear phase matching. If ω_i's are far away from absorption, this can be achieved in anisotropic crystals by requiring one or two $\vec{E}(\omega_i)$ to be ordinary rays and the rest extraordinary. In this respect, one scheme is particularly worth mentioning. Consider a given set of ω_i. We may vary the temperature of the crystal to change k_i sufficiently so that phase matching appears in the direction perpendicular to the $\hat{c}$ axis (Boyd and Kleinman, 1968), as shown in Fig. 3(b) for the case of second-harmonic generation. Now, unlike phase matching in other directions, the phase-matching condition is still approximately satisfied when the beam propagation slightly deviates from the direction perpendicular to $\hat{c}$. This is important since we can then use a focused pump beam to increase the pump field intensity, and hence the conversion efficiency, without appreciably affecting the phase-matching condition. The beam wall-off problem is also minimized because along a principal axis the wave vector and the Poynting vector are parallel to each other. The 90° phase matching with temperature tuning has now been widely used.

The technology of constructing second-order nonlinear optical devices has become more and more mature. Parametric oscillators using the second harmonic of a Nd:YAG laser as the pump source are commerically available (e.g., Chromatix, Inc., Mountain View, Calif.). Their output can be tuned from 5480 Å to 3.65 μm. Successful operation of parametric oscillators with output further down in the infrared have also been reported (Herbst and Byer, 1971; Hanna *et al.*, 1972; Hanna *et al.*, 1974). The output waves $\vec{E}(\omega_2)$ and $\vec{E}(\omega_3)$ from the

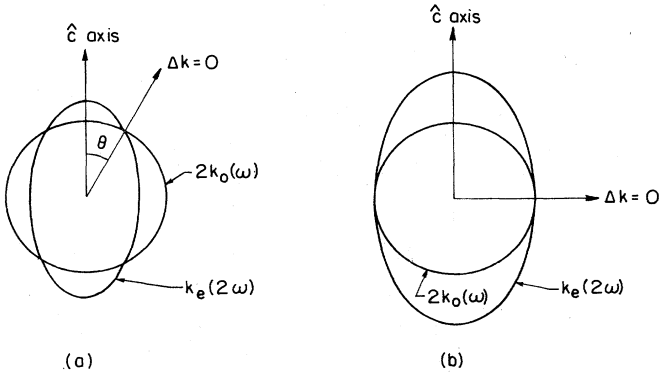

FIG. 3. Plots of the ordinary wave vector $2k_0(\omega)$ and the extraordinary wave vector $k_e(2\omega)$ in the plane containing the $\hat{c}$ axis of a negative uniaxial crystal. At phase matching, $\Delta k = 2k_0(\omega) - k_e(2\omega) = 0$. Phase-matching direction is (a) at an angle θ and (b) at 90° with respect to the $\hat{c}$ axis. It is seen that, for the 90° phase-matching case, $\Delta k = 0$ is approximately satisfied for beams propagating within a fairly large angle around the phase-matching direction.

oscillator can again be used to mix with each other or with the pump field $\vec{E}(\omega_1)$ in another nonlinear crystal to generate tunable sum- or difference-frequency fields. Using such a scheme, Herbst and Byer (1975; see also Byer *et al.*, 1974) have recently constructed a system which is capable of producing a collimated coherent light beam tunable from ~2500 Å to ~30 μm.

A more recent advance in second-order nonlinear optics is in difference-frequency generation of tunable infrared, in particular far-infrared radiation. As is well known, the field of far-infrared spectroscopy has suffered badly because of lack of intense tunable sources. A 10-msr beam radiated from a 1-cm^2 blackbody at 5000 °K contains only 1.5×10^{-8} W of far-infrared power around 50 cm^{-1} with a spectral purity of 1 cm^{-1}. It now seems possible that one can obtain much more powerful far-infrared radiation simply by mixing two tunable laser beams in a nonlinear crystal (Faries *et al.*, 1969; Faries *et al.*, 1971; Yajima and Inoue, 1968 a, b; 1969; Chang *et al.*, 1968; Bridges and Chang, 1969; Patel and Nguyen, 1969; Nguyen and Patel, 1969; Bridges and Stonad, 1972; Boyd *et al.*, 1972; Nguyen and Bridges, 1972; Bridges and Nguyen, 1973; Yang *et al.*, 1973; Lax *et al.*, 1973; Lee *et al.*, 1974; Brignall *et al.*, 1974; Nguyen and Bridges, 1975). With pulsed dye lasers, the infrared output can in principle be tuned from 0 to ~10 000 cm^{-1}, limited only by the absorption band of the crystals (Yang *et al.*, 1973; Dekker and Tittel, 1973). With CO_2 lasers, the far-infrared output can be discretely tuned between 5 and 140 cm^{-1} in 3200 steps (Lax *et al.*, 1973). Even with reasonable pump power, the peak power of the far-infrared output at ~10 cm^{-1} can be more than 100 mW. More recently, using the multiple total-reflection scheme, Lee *et al.* (1974) have been able to obtain, with two 25-W CO_2 laser beams mixed in GaAs, a cw far-infrared radiation of 10^{-7} W (Lax and Aggarwal, 1974). With the GaAs crystal forming a dielectric waveguide for the far-infrared radiation, Thompson and Coleman (1974) have observed a maximum conversion efficiency of 20% of the predicted value. It has also been demonstrated recently that tunable far-infrared radiation can be obtained by difference-frequency generation via spin-flip Raman transitions in a crystal (Nguyen and Bridges, 1972; Bridges and Nguyen, 1973; Brignall *et al.*, 1974). We shall postpone the discussion of this particular subject to Sec. V on stimulated Raman transitions.

IV. OPTICAL MIXING IN VAPOR

In a vapor system, $\vec{\chi}^{(2)}$ vanishes in the electric-dipole approximation because of inversion symmetry. The next higher-order nonlinearity is described by $\vec{\chi}^{(3)}$. Since it is of higher order, one normally would expect $\vec{\chi}^{(3)}$ to be so small that the corresponding nonlinear optical effects would be insignificant. This is particularly true for a vapor system with a low density of atoms or molecules. However, when the optical frequencies are close to strong resonances, the case is quite different. Because of resonant enhancement, $\vec{\chi}^{(3)}$ can actually become so large that the third-order nonlinear optical processes in a vapor can appear as strong as the second-order processes in a crystal. The atomic vapor systems are particularly attractive. Their sharp, discrete transitions are strong and well understood, and the absence of rotational and vibrational states greatly reduces the number of possible optical transitions.

Over the past few years, a number of very interesting third-order optical mixing processes in atomic vapor have been reported. The atomic systems now appear to be the only media one can use to generate far-uv or perhaps even soft x-ray radiation by nonlinear optical means (Miles and Harris, 1971; Young *et al.*, 1971; Kung *et al.*, 1972; Kung *et al.*, 1973; Harris, 1973; Harris *et al.*, 1973). Via optical mixing, they can also be used to construct tunable uv generators (Hodgson *et al.*, 1974), tunable infrared generators (Sorokin *et al.*, 1973; Wynne *et al.*, 1973), and infrared up-converters (Harris and Bloom, 1974; Bloom *et al.*, 1974). In the following, we shall use potassium vapor to illustrate the various third-order processes. The principles can of course be applied to other vapor systems.

In Fig. 4, we show the energy level diagram of K. Consider first the third-harmonic generation as indicated in Fig. 4(a). It is easy to show by third-order perturbation that $\vec{\chi}^{(3)}$ is given by (Miles and Harris, 1973)

$$\vec{\chi}^{(3)} = (Ne^4/\hbar^3)\sum_{g,a,b,c} \vec{r}_{ga}\vec{r}_{ab}\vec{r}_{bc}\vec{r}_{cg}A_{abc},$$

$$\begin{aligned} A_{abc} = {} & [(\omega_{ag}-3\omega)(\omega_{bg}-2\omega)(\omega_{cg}-\omega)]^{-1} \\ & + [(\omega_{ag}+\omega)(\omega_{bg}+2\omega)(\omega_{cg}+3\omega)]^{-1} \\ & + [(\omega_{ag}+\omega)(\omega_{bg}+2\omega)(\omega_{cg}-\omega)]^{-1} \\ & + [(\omega_{ag}+\omega)(\omega_{bg}-2\omega)(\omega_{cg}-\omega)]^{-1}, \end{aligned} \tag{4.1}$$

where $\vec{r}_{ij}\equiv\langle i|\vec{r}|j\rangle$, the subscript g denotes the ground states, the subscripts a, b, and c denote the excited states, and $\hbar\omega_{ij}$ is the energy difference between states $\langle i|$ and $\langle j|$. For simple atomic systems, both $\vec{r}_{ij}$ and ω_{ij} are either tabulated (see, for example, Weiss *et al.*, 1969) or calculable (Condon and Shortley, 1951). For an isotropic medium, the electronic $\vec{\chi}^{(3)}(3\omega)$ has only one nonzero independent element which is $\chi^{(3)}_{1111}$ in the conventional notation. In Fig. 5, we show the variation of $|\chi^{(3)}(3\omega)|$ as a function of incident wavelength ($\lambda=2\pi c/\omega$) (Miles and Harris, 1973). It is seen that when ω, or 2ω, or 3ω approaches resonance, $|\chi^{(3)}|$ undergoes a strong resonant enhancement. At ~10 cm^{-1} away from resonance, we have $|\chi^{(3)}|/N\sim10^{-31}$ esu. Thus, if we have a system with $N\sim10^{17}$ cm^{-3} and a laser beam of $|E|\sim10^4$ esu (corresponding to an intensity of 2.5×10^{10} W/cm^2), we would find a nonlinear polarization of $\chi^{(3)}|E|^3\sim10^{-2}$ esu. This can be compared with a nonlinear polarization of $\chi^{(2)}|E|^2\sim10^{-3}$ esu in a solid with $\chi^{(2)}\sim10^{-7}$ esu and $|E|\sim10^2$ esu (2.5×10^6 W/cm^2). Note that the optical breakdown threshold in solids is usually much lower than in gases. The maximum laser intensity allowed in alkali vapor, as limited by multiphoton ionization, is in the range 10^{10}–10^{12} W/cm^2 (Miles and Harris, 1973).

In order to have efficient third-harmonic generation, we must not only have large $\chi^{(3)}$ but also have phase matching in the medium. With a beam of finite cross section, collinear phase matching, $k(3\omega)=3k(\omega)$ or

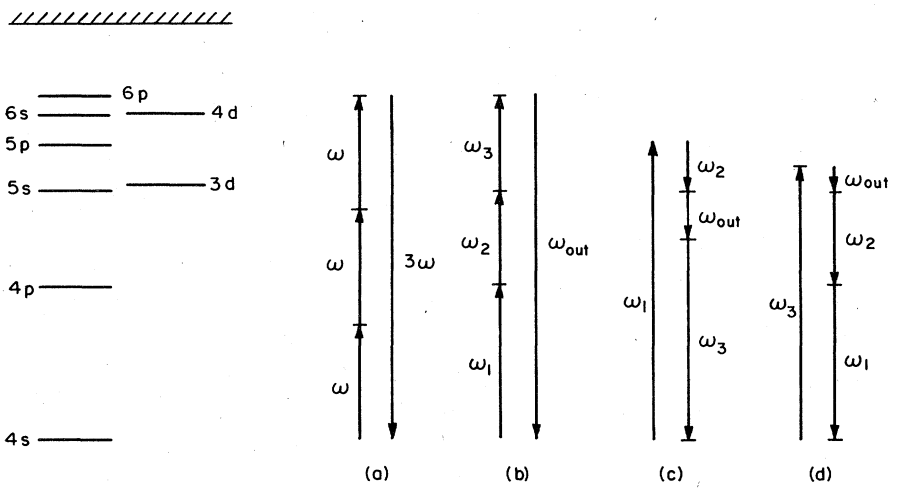

FIG. 4. Energy level diagram of a potassium atom and sketch for a number of resonant third-order optical mixing processes. (a) Third-harmonic generation; (b) sum-frequency generation with ω_1, $\omega_1+\omega_2$, and $\omega_1+\omega_2+\omega_3$ near resonances; (c) infrared generation with ω_1 and $\omega_1-\omega_2$ near resonances; (d) infrared generation with ω_1 and $\omega_1+\omega_2$ near resonances.

$\chi^{(1)}(3\omega)=\chi^{(1)}(\omega)$, can yield a much longer effective interacting length. In a vapor system with a given ω, this can be achieved only with the help of a buffer gas. By choosing an appropriate buffer gas and using its density as a variable, we may then satisfy the phase-matching relation (Miles and Harris, 1973)

$$\chi^{(1)}_{\text{vapor}}(\omega)+\chi^{(1)}_{\text{buffer}}(\omega)=\chi^{(1)}_{\text{vapor}}(3\omega)+\chi^{(1)}_{\text{buffer}}(3\omega)\,. \tag{4.2}$$

In this case, similar to the 90°-phase-matching case in solids, one can use optimum focusing to help achieve higher conversion efficiency. Limitations on the laser intensity and the atomic density have been discussed in detail by Miles and Harris (1973).

Using such a scheme, Young *et al.* (1971) have shown that conversion of 1.06 μm → 3547 Å in a mixture of Rb vapor and Xe can have an efficiency of 10–20% (Bloom *et al.*, 1975). Kung *et al.* (1971; 1973) have demonstrated third-harmonic generation of vacuum uv radiation up to 887 Å in Cd:Ar mixtures and in Xe:Ar inert gas mixtures with ~3% conversion efficiency. Vacuum uv generation by the 5th-harmonic process in an inert gas mixture has also been proposed (Harris, 1973) and realized (Harris *et al.*, 1973; 1974). It is hoped that the technique can be extended to produce coherent radiation of soft x rays at wavelengths as short as 177 Å (5th harmonic of 887 Å).

In the above scheme there are two apparent shortcomings. First, with ω being the only frequency variable, $|\chi^{(3)}(3\omega)|$ is generally limited by single-resonance enhancement, i.e., we usually do not find ω, 2ω, and 3ω simultaneously near resonance. Second, only in narrow frequency regions, $|\chi^{(3)}(3\omega)|$ is large because of resonant enhancement. These limitations can be avoided if we do not require the three incoming photons to be of the same frequency.

Let us now consider the more general case of optical mixing with $\omega_1+\omega_2+\omega_3=\omega_{\text{out}}$ for uv generation. As shown in Fig. 4(b), we can have ω_1, $\omega_1+\omega_2$, and $\omega_1+\omega_2+\omega_3$ simultaneously close to resonance. The corresponding third-order susceptibility $\vec{\vec{\chi}}^{(3)}$ is now dominated by the resonant term

$$\vec{\vec{\chi}}^{(3)}\cong(Ne^4/\hbar^3)\sum_{s,p}\vec{r}_{4s,4p}\vec{r}_{4p,5s}\vec{r}_{5s,5p}\vec{r}_{5p,4s}A_{sp}\,,$$

$$A_{sp}=[(\omega_{4p}-\omega_1+i\Gamma_{4p})(\omega_{5s}-\omega_1-\omega_2+i\Gamma_{5s})\times(\omega_{5p}-\omega_1-\omega_2-\omega_3+i\Gamma_{5p})]^{-1}\,, \tag{4.3}$$

where $\sum_{s,p}$ is over the fine structures of the s and p states, and Γ's are the phenomenological damping constants. Assuming $N\sim10^{17}$ cm^{-3} and each frequency factor in A_{sp} to be 1 cm^{-1}, we can already have $|\chi^{(3)}|\sim3\times10^{-10}$ esu or $|\chi^{(3)}|/N\sim3\times10^{-27}$ esu. With such a large $|\chi^{(3)}|$, the third order sum-frequency generation should be easily observable even if the pump beam intensities are low. The maximum pump intensity in this case would presumably be limited by single and multiphoton absorption and other induced nonlinear optical processes. Hopefully, one can again use appropriate buffer gas to achieve phase matching.

The above scheme is essentially what Hodgson *et al.* (1974) used to obtain tunable vacuum uv radiation with dye lasers. They chose the Sr vapor system instead of alkali vapor because of the existence of strong discrete autoionization levels of alkali earth atoms in the vacuum uv range. An N_2 laser was used to pump simultaneously two dye lasers, one at frequency ω_1 and the other at ω_2. With ω_1 and ω_2 both variable, tunable uv output at $2\omega_1+\omega_2$ from Sr vapor was observed over a spectral range of several thousand cm^{-1}. In this case, ω_1 and $2\omega_1+\omega_2$ could be considered as near resonance, but did not need to be very close to any discrete resonance. When either 2ω or $\omega_1+\omega_2$ was tuned to a double-quantum allowed transition from the ground $(5s)^2$ state to an even-parity excited state of Sr, large enhancement in the output intensity at $2\omega_1+\omega_2$ was seen. The enhancement should of course be even stronger if in addition either ω_1 or $2\omega_1+\omega_2$ or both are also very close to resonance. This was experimentally demonstrated when $2\omega_1+\omega_2$ was tuned over the autoionizing states. It now provides a new method for studying the properties of autoionizing states of atoms (Armstrong and Wynne, 1974).

We now consider another interesting third-order optical mixing process in atomic vapor, namely, tunable

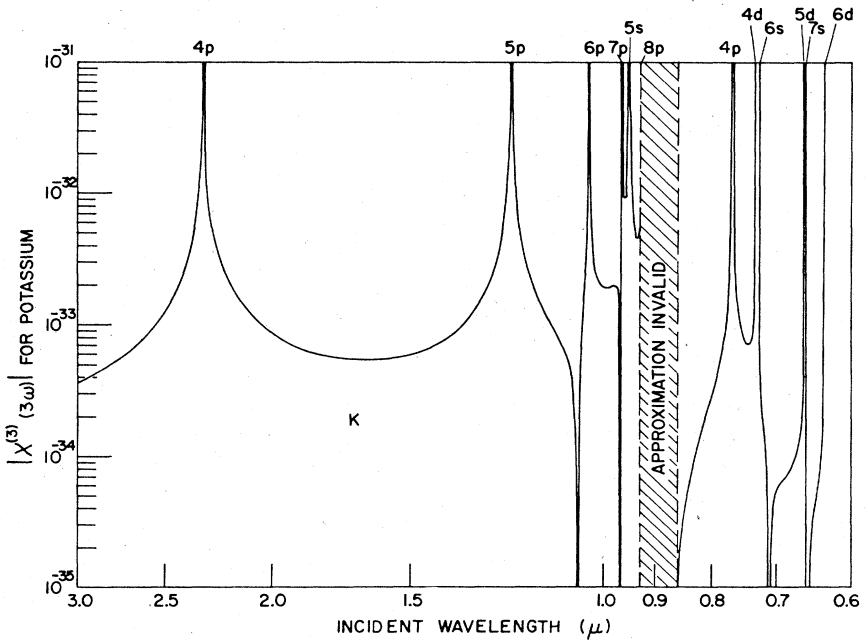

FIG. 5. Variation of $|\chi^{(3)}(3\omega)|$ as a function of the incident laser wavelength ($\lambda = 2\pi c/\omega$) for potassium. Resonant enhancement peaks are due to ω, 2ω, or 3ω near resonances with various transitions, as indicated (after Miles and Harris, 1973).

infrared generation (Sorokin *et al.*, 1973; Wynne *et al.*, 1973). In Fig. 4(c) we show the transition process in which the infrared radiation at $\omega_{out} = \omega_1 - \omega_2 - \omega_3$ is generated by the pump fields at ω_1, ω_2, and ω_3. Both ω_1 and $\omega_1 - \omega_2$ are close to resonance. The third-order susceptibility is given by

$$\vec{\chi}^{(3)} \cong (Ne^4/\hbar^3) \sum_{s,p} \vec{r}_{4s,5p}\vec{r}_{5p,5s}\vec{r}_{5s,4p}\vec{r}_{4p,4s} A_{sp} ,$$

$$A_{sp} = [(\omega_{5p} - \omega_1 + i\Gamma_{5p})(\omega_{5s} - \omega_1 + \omega_2 + i\Gamma_{5s})(\omega_{4p} - \omega_3)]^{-1} . \tag{4.4}$$

Again, because of resonant enhancement, $|\chi^{(3)}|$ can be of the order of 10^{-10} esu or larger. With ω_1 and ω_2 fixed and ω_3 varied, the infrared output can in principle be tuned over a very wide spectral range (0 to ~10 000 cm^{-1}) if it is not limited at long wavelengths by diffraction and radiation efficiency. This has actually been observed by Sorokin *et al.* (1973; see also Wynne *et al.*, 1973). In their experiment, they used two dye lasers, one at ω_1 and the other at ω_3. When ω_1 was close to ω_{5p} of K atoms, stimulated Raman oscillation from (4s) to (5s) occurred in the vapor system, generating an intense Stokes radiation at ω_2. Subsequently, optical mixing of fields at ω_1, ω_2, and ω_3 in K vapor produced the infrared radiation at $\omega_1 - \omega_2 - \omega_3$.[2] They used anomalous dispersion with the help of buffer gas to achieve phase matching. The infrared radiation had a tuning range of 2–25 μm. Starting with a 100 kW N_2 laser to pump the dye lasers, they obtained a peak power of 100 mW at 2 μm.

Another scheme to generate tunable infrared radiation in atomic vapor is shown in Fig. 4(d). Here, we let ω_1 be close to a single-photon transition and $\omega_1 + \omega_2$ close to a double-photon transition from the ground state. Then $|\chi^{(3)}(\omega_{ir} = \omega_3 - \omega_1 - \omega_2)|$ is again large. With ω_3 being a variable, tunable infrared radiation at $\omega_{ir} = \omega_3 - \omega_1 - \omega_2$ can be easily generated. This scheme has not yet been tried out experimentally. A closely related process is also of interest. We can interchange the roles of fields at ω_3 and ω_{ir} with $\omega_3 = \omega_1 + \omega_2 + \omega_{ir}$ being the output frequency (Harris and Bloom, 1974; Bloom *et al.*, 1974). By symmetry, we have $|\chi^{(3)}(\omega_3 = \omega_1 + \omega_2 + \omega_{ir})| = |\chi^{(3)}(\omega_{ir} = \omega_3 - \omega_1 - \omega_2)|$. As a result, we should again expect such a third-order process to be strong. This is in fact a process one can use to construct an effective infrared-to-visible up-converter. Bloom *et al.*, (1974) have employed essentially such a scheme to achieve infrared-to-uv up-conversion. With a pump power of 3 kW and an infrared power of 5 mW in Na vapor, they have already achieved a power conversion efficiency of 1620% (corresponding to a photon conversion efficiency of 58%). It appears that the construction of a practical infrared image converter based on this effect may be quite possible.

There are of course a number of other variations of third-order optical mixing processes in atomic vapor. For example, we can have infrared generation by the process $\omega_{ir} = \omega_1 + \omega_2 - \omega_3$ with both ω_1 and $\omega_1 + \omega_2$ close to resonances of allowed transitions. So far, experimental effort on this subject has certainly not exhausted all the possibilities yet. We have not discussed here stimulated Raman scattering and parametric processes in metal vapor. The readers are referred to articles by Barak *et al.* (1969), Sorokin and Lankard (1973), and Carlsten and Dunn (1975).

V. STIMULATED RAMAN SCATTERING

Stimulated light scattering is a special class of third-order nonlinear optical effects. Usually, to each case of spontaneous emission or scattering, there is a cor-

[2]More correctly, the process should be considered as a four-wave parametric amplification process in which the pump waves are at ω_1 and ω_3 and the signal and idler waves are at ω_2 and ω_{out}. The Stokes radiation at ω_2 and the infrared radiation at ω_{out} grow together in the process.

responding case of stimulated emission or scattering. In a scattering process, a photon at $\omega_1(\vec{k})$ is absorbed and a photon at $\omega_2(\vec{k}_2)$ is emitted while the material makes a transition from the initial state $|i\rangle$ to the final state $|f\rangle$. The material excitation involved can be an entropy wave (Rayleigh scattering), a pressure wave (Brillouin scattering), a phonon, magnon, plasmon, or electronic excitation (Raman scattering), a concentration variation in a mixture (concentration scattering), etc. The transition probability W_{fi} per unit time per unit volume from $|i\rangle$ to $|f\rangle$ can be obtained from perturbation calculation and is proportional to $m_1(\omega_1,\vec{k})[m_2(\omega_2,\vec{k}_2)+1]$ (see, for example, Heitler, 1954), where $m_1(\omega_1,\vec{k}_1)$ and $m_2(\omega_2,\vec{k}_2)$ denote the numbers of photons in the incoming and the scattered radiation modes, respectively. Spontaneous scattering corresponds to $m_2=0$ and stimulated scattering to $m_2\neq 0$.

From intuitive physical argument, the amplification rate of $m_2(\omega_2,\vec{k}_2)$ in space due to stimulated scattering is given by

$$\frac{dm_2}{dz}=\left(\frac{dW_{fi}}{d\omega_2}\rho_i-\frac{dW_{if}}{d\omega_2}\rho_f\right)n_2/c-\alpha_2 m_2\,, \tag{5.1}$$

where ρ_i and ρ_f are the populations of $|i\rangle$ and $|f\rangle$, respectively, n_2 is the refractive index, and α_2 is the absorption coefficient at ω_2. We can write $dW_{fi}/d\omega_2=A(\omega_1,\omega_2)m_1(m_2+1)$ and $dW_{if}/d\omega_2=A(\omega_1,\omega_2)m_2(m_1+1)$. If $m_1,m_2\gg 1$, then Eq. (5.1) becomes

$$dm_2/dz=(G-\alpha_2)m_2\,, \tag{5.2}$$

where $G=An_2(\rho_i-\rho_f)m_1/c$. The solution of Eq. (5.2) is $m_2(z)=m_2(0)\exp[(G-\alpha_2)z]$ if $m_1(\omega_1,\vec{k}_1)$ can be taken as a constant. Thus, as long as $G>\alpha$, we expect to find initially an exponential growth of the scattered radiation until depletion of $m_1(\omega_1,\vec{k}_1)$ into $m_2(\omega_2,\vec{k}_2)$ or saturation sets in. This is characteristic of stimulated scattering. It has, however, been shown that Eqs. (5.1) and (5.2) do not really describe stimulated scattering correctly when the dispersion of the material excitation is non-negligible (Shen and Bloembergen, 1965). A coupled wave approach becomes more proper.

Here we shall limit our discussion to stimulated Raman scattering (SRS), since this is the area where we have had more important new development. The Raman gain G is usually small. In liquids, for example, G is of the order of 10^{-2} cm^{-1} per MW/cm^2 of laser excitation. In order to generate e^{30} Raman photons from noise in a 1-cm path length, we need a laser beam with an intensity of 3 GW/cm^2. Therefore, SRS can only be observed with a high-power laser beam. It has, however, been seen in some liquids at a much lower power level. In these cases, SRS is actually initiated by self-focusing of the laser beams, and the apparently lower threshold corresponds to the self-focusing threshold (Wang, 1966; Loy and Shen, 1971). We shall discuss self-focusing in detail in Sec. VI.

Early interest in SRS arose because it could provide intense coherent radiation at new frequencies and because it was a possible loss mechanism in high-power laser transmission. Recently it has been demonstrated that tunable radiation, even in the far infrared, can be generated by SRS. SRS can also be used as a nonlinear spectroscopic tool to probe the low excitation levels and to determine the third-order nonlinearity of a medium. It is presently the only method to measure directly the vibrational relaxation times of liquid and solids. There already exist in the literature several review articles on stimulated Raman scattering (Bloembergen, 1967; Kaiser and Maier, 1972; Shen, 1975). Here, we shall describe only briefly the more recent developments.

For a better understanding of various aspects of stimulated scattering, we should use the coupled-wave approach (Shen and Bloembergen, 1965; Shen, 1973; 1975). The excitation from $\langle i|$ to $\langle f|$ can be described by a wave ψ driven by the beat of two em waves, with a possible change of populations in $\langle i|$ and $\langle f|$. The problem then appears to be similar to parametric amplification. Here, however, the signal and idler waves consist of one em wave and one material excitational wave. Let $E_l\sim\exp(-i\omega_l t)$ and $E_s\sim\exp(-i\omega_s t)$ be the laser and the Stokes Raman fields, respectively, and $\psi\sim\exp[-i(\omega_l-\omega_s)t]$. Then the three nonlinearly coupled wave equations are

$$\mathcal{L}_E(\omega_l)E_l=\frac{4\pi\omega_l^2}{c^2}P_l^{NL},\quad \mathcal{L}_E(\omega_s)E_s=\frac{4\pi\omega_s^2}{c^2}P_s^{NL},\quad \mathcal{L}\psi=f\,, \tag{5.3}$$

where $\mathcal{L}_E$ and $\mathcal{L}$ are differential operators for the waves E and ψ, respectively,

$$P_l^{NL}=-\partial F/E_l^*,\quad P_s^{NL}=-\partial F/\partial E_s^*,\quad f=-\partial F/\partial N(\rho_i-\rho_f)\psi^*\,, \tag{5.4}$$

and $F=NME_lE_s^*\psi^*(\rho_i-\rho_f)+\text{c.c.}$ can be regarded as the average nonlinear coupling energy. N is the number of molecules or unit cells per unit volume, M is a coupling constant, and ρ_i and ρ_f are the populations in $\langle i|$ and $\langle f|$, respectively. When the Raman transition probability is high, ρ_i and ρ_f can have appreciable change during the Raman process. With $\Delta\rho\equiv\rho_f-\rho_f^0=-(\rho_i-\rho_i^0)$, where ρ_i^0 and ρ_f^0 are the thermal equilibrium populations, we have

$$(\partial/\partial t+1/T_1)\Delta\rho=\tfrac{1}{2}i\omega_{fi}[NME_lE_s^*\psi^*-\text{c.c.}](\rho_i-\rho_f)\,, \tag{5.5}$$

where T_1 is the relaxation time, and ω_{fi} is the frequency separation between $\langle f|$ and $\langle i|$. In case ρ_i and ρ_f are constant, the solution of Eq. (5.3) is similar to that for parametric amplification (see, for example, Bloembergen, 1965). As expected, the gain (or the energy transfer) is a maximum when the momentum conservation (or phase matching) $\vec{k}_l=\vec{k}_s+\vec{k}_\psi$ is satisfied. If ψ is dispersionless, and $|E_l|$ can be approximated as a constant, we can then easily show that $|E_s(z)|^2=|E_s(0)|^2\times\exp[(G-\alpha)z]$, which agrees with the solution of Eq. (5.2). The more general solution, taking into account the depletion of $|E_l|^2$, can also be obtained easily.

There are a number of material excitational waves which can be considered as dispersionless in SRS, e.g., molecular vibration, optical phonon, plasmon, electronic level excitation, etc. Most research work in the past has been concentrated on stimulated Raman scattering by molecular vibrations or optical phonons. More recently, attention has been drawn to the case of SRS by electronic excitations, in particular between two Zeeman-split levels. The latter is known as stimulated spin-flip Raman scattering (SSRS) (Patel and Shaw, 1970; 1971). The

Stokes output can be tuned by adjusting the Zeeman splitting with an applied magnetic field.

SSRS has been observed in InSb (Patel and Shaw, 1970; 1971), InAs (Eng *et al.*, 1974), and HgTe (Sattler *et al.*, 1974). The case of InSb has been most thoroughly investigated. Because of its large g factor (~50), the Zeeman splitting of its Landau levels can vary from 0 to 250 cm^{-1} by varying the magnetic field from 0 to 100 kG. The spin-flip Raman gain G in InSb is also extremely high. We find $G = 1.7\times10^{-5} I$ cm^{-1} in an n-type InSb with $n = 3\times10^{16}$ cm^{-3} where I is the CO_2 laser intensity in W/cm^2 at 10.6 μm. The gain can be increased even further via resonant enhancement by moving the laser frequency closer towards the band gap (Mooradian *et al.*, 1970; Brueck and Mooradian, 1971). For example, with a CO laser at 5.3 μm, the gain becomes $G = 6\times10^{-4} I$ cm^{-1}.

Patel and Shaw (1970; 1971) first observed SSRS in InSb with a Q-switched CO_2 laser at 10.6 μm. They were able to tune the output from 10.9 to 13.0 μm. The output linewidth was less than 0.03 cm^{-1}. This then provides a practical tunable coherent source in the infrared. Using a single-mode CO laser at 5.3 μm, Breuck and Mooradian (1970; 1971) showed that SSRS could even be operated on a cw basis. They obtained a pump threshold of less than 50 mW, a power conversion efficiency of larger than 50%, and an output power in excess of 1 W. The output linewidth was found to be less than 1 kHz (Patel, 1972).

As we mentioned earlier, stimulated Raman scattering resembles parametric amplification. Both E_s and ψ are amplified in the process. In general, the excitational wave ψ can also be a composite wave. For example, it can be a polariton wave which is a linear combination of electromagnetic and material excitational waves resulting from direct coupling of the two waves (Huang, 1951 a,b). This is the case when the material excitation can be directly excited by a one-photon process. Thus, in the output of SRS by polaritons, there are two electromagnetic waves (see, for example, Shen, 1965; Henry and Garrett, 1968), one at the Stokes frequency $\omega_s(\vec{k}_s)$ and the other at the polariton frequency $\omega_p = \omega_l - \omega_s$ (with $\vec{k}_p = \vec{k}_l - \vec{k}_s$).

In Fig. 6 we show two possible polariton dispersion curves $\omega_p(k_p)$. Curves (a) and (b) correspond, respectively, to weak and strong coupling between em and material excitational waves. The former describes well the spin-flip case where the spin-flip transitions can be weakly excited by infrared radiation. We would therefore expect to find radiation at both ω_s and ω_p in the output of SSRS. However, in order to have strong output at ω_p, we must have both a large Raman gain and a large em proportion in the polariton wave at ω_p. This happens around the knee of the polariton dispersion curve. Since the Zeeman splitting can be tuned by an external magnetic field, there now exists a potential coherent source which is tunable at both ω_s and ω_p (Shen, 1973).

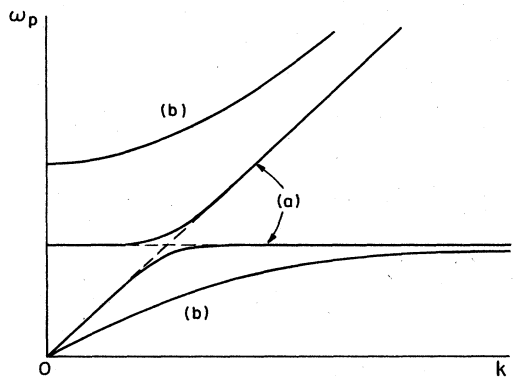

FIG. 6. Polariton dispersion curves. (a) Weak coupling and (b) strong coupling between electromagnetic and material excitational waves.

No observation of far-infrared output from SSRS has yet been reported. It is, however, possible to obtain tunable far-infrared output at the Zeeman-split frequency by feeding both the laser and the Stokes beams into the crystal. This has indeed been seen in InSb (Nguyen and Bridges, 1972; 1975) and the results agree well with the theory sketched here. It is believed that SSRS in InSb can yield a practical coherent far-infrared source tunable over a range of 200 cm^{-1} with an extremely narrow linewidth.

Curve (b) of Fig. 6 describes the polariton dispersion of an infrared-active phonon branch. In this case, the output of SRS can also be tuned by adjusting the relative angle between $\vec{k}_l$ and $\vec{k}_s$ with ω_p changing along the polariton dispersion curve so that $\vec{k}_l(\omega_l) = \vec{k}_s(\omega_s) + \vec{k}_p(\omega_p)$. The tuning range depends mainly on the shape of the polariton curve. In $LiNbO_3$, SRS by polaritons of the 248 cm^{-1} phonon mode has been observed with a 1-MW Q-switch ruby laser (Kurtz and Giordmaine, 1969; Gelbwachs *et al.*, 1969). The frequency ω_p can be tuned from 50 to 238 cm^{-1}. In a resonator, up to 70% of the laser power can be converted into Stokes. A far-infrared output at ω_p with a 5-W peak power has also been observed (Yarborough *et al.*, 1969; Piestrup *et al.*, 1975). This, therefore, gives another potential far-infrared source which is coherent and tunable.

More generally, in SRS, the waves at ω_p can also beat with the em waves at ω_l and ω_s to create an antiStokes field at $\omega_a = \omega_l + \omega_p$ and the second-order Stokes field at $\omega_{2s} = \omega_s - \omega_p$. In a similar fashion, higher-order Stokes and antiStokes fields can be generated. Both Stokes and antiStokes radiation of many orders can be easily observed in SRS in the presence of self-focusing. In SSRS and in InSb, Stokes and antiStokes radiation up to the fourth order have been observed (DeSilets and Patel, 1973).

In most cases, pulsed lasers are used to study SRS. If the laser pulse width is shorter than, or comparable with, the relaxation times of the material excitation, then we should expect a transient SRS. Two different relaxation times are connected with a material excitation. The longitudinal relaxation time T_1 governs the decay of the population difference $\Delta\rho = \rho_f - \rho_f^0$, as shown in Eq. (5.5). The transverse relaxation time T_2 governs the decay of the excitational wave ψ. The theory of transient SRS has been worked out by a number of authors (see, for example, Carman *et al.*, 1970) and has recently been checked experimentally (Carman and Mack, 1972; Lowdermilk and Kachen, 1975; Kachen, 1975).

Usually in condensed matter, T_1 and T_2 are in the picosecond range. Therefore transient SRS occurs when a

high-power picosecond pulse propagates in the medium. Both $\Delta\rho$ and ψ get excited in the process and then decay with T_1 and T_2, respectively, after the pulse is gone. If we now send another picosecond probe pulse at ω_l' into the medium, it will lead to a spontaneous antiStokes emission at $\omega_l' + \omega_{fi}$ in all directions due to the presence of $\Delta\rho$, and a coherent antiStokes field at $\omega_l + \omega_l' - \omega_s$ in the direction of $\vec{k}_l + \vec{k}_l' - \vec{k}_s$ as a result of beating with ψ. The incoherent spontaneous antiStokes emission is proportional to $\Delta\rho(t)$ and the coherent antiStokes field is proportional to $\psi(t)$. By varying the time delay between the two picosecond pulses at ω_l and ω_l' and measuring the corresponding intensity variations of both the incoherent and the coherent antiStokes radiation, one can find T_1 and T_2. This turns out to be the only existing method for measuring the vibrational relaxation times of liquids and solids, as demonstrated by Alfano and Shapiro (1971), and by Kaiser and his associates (von der Linde *et al.*, 1971; Laubereau *et al.*, 1971; 1972; 1973; Laubereau and Kaiser, 1974). An example of their results is shown in Fig. 7. In principle, the same measurements can be done by exciting the material excitation directly with an infrared picosecond pulse if the excitation is allowed by the selection rule (Laubereau and Kaiser, 1974). Using spontaneous antiStokes emission at various frequencies to monitor the populations of various excited states, one can also study the decay route of a particular excitation (Alfano and Shapiro, 1972; Laubereau *et al.*, 1973; Laubereau *et al.*, 1974).

Coherent antiStokes emission can also be used as a nonlinear spectroscopic technique to probe resonant structure in the near and far infrared. From the results, the sign and the magnitude of the third-order electronic nonlinearity can also be deduced. The method will be discussed in detail in Sec. VII. It has excellent sensitivity especially when the resonant structure is narrow and has been proposed as a means for detection of low-concentration substances in a gas mixture.

A number of other applications of SRS have also been considered. It has been proposed as a possible means to heat a plasma for controlled fusion work (Cohen *et al.*, 1973). When a laser beam at ω_l and a broadband radiation at higher frequencies are simultaneously incident on a medium, absorption lines at frequencies $\omega_l + \omega_p$ may show up in the broadband spectrum because of SRS, where ω_p is the frequency of a Raman mode. This effect, known as the inverse Raman effect (Jones and Stoicheff, 1964; McQuillan and Stoicheff, 1966; McLaren and Stoicheff, 1970), can be seen with picosecond pulses (Alfano and Shapiro, 1971), and may be used for Raman spectroscopy. SRS is also a limiting factor for transmission of high-power laser beams in materials. Finally, using a tunable dye laser as the pump source, SRS in high-pressure gas cells provides a tunable infrared source in the near infrared down to ~2000 cm^{-1} (Frey and Pradere, 1974; Schmidt and Apt, 1972, 1974).

Among other types of stimulated light scattering, we shall only mention stimulated Compton scattering. Pantell *et al.* (1968) first proposed the generation of tunable far-infrared radiation by backscattering microwaves from a relativistic electron beam. Tunability could be achieved by varying the electron energy. Recently, Sukhatme and Wolff (1974) showed that stimulated Compton scattering could be greatly enhanced in a magnetic field if the microwave frequency is equal to the cyclotron resonance frequency. Experiments on stimulated Compton scattering have not yet been performed. However, with a somewhat similar experimental arrangement, tunable microwave and far-infrared radiation has been seen from relativistic electrons performing cyclotron motion in a magnetic field (Granastein *et al.*, 1974). Intense microwave emission (with a peak power of 500 MW and a conversion efficiency of 17%) has also been observed in coherent Cherenkov radiation from a relativistic electron beam interacting with a slow-wave structure (Carmel *et al.*, 1974).

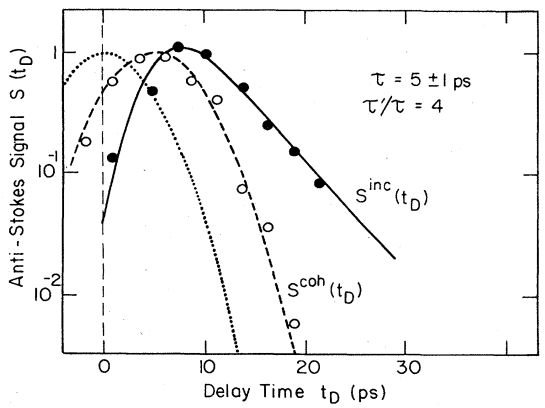

FIG. 7. Measured incoherent scattering signal $S^{inc}(t_D)/S^{inc}_{max}$ (closed circles) and coherent scattering signal $S^{coh}(t_D)/S^{coh}_{max}$ (open circles) versus delay time t_D between the exciting and the probe pulses in 1, 1, 1-trichlorethane. The solid and dashed curves are theoretical curves used to fit the data. The dotted lines indicate the pump pulse (after Laubereau *et al.*, 1972).

VI. SELF-FOCUSING OF LIGHT

A well-known third-order nonlinear optical effect of great interest is the phenomenon of self-focusing of light. Early in 1964, Herscher (1964) found that a focused laser beam of a few megawatts would induce long tracks of damage spots of several μm in diameter in a solid. Chiao *et al.* (1964) proposed that self-focusing and self-trapping were responsible for the damage tracks. Askar'yan (1962) and Talanov (1964) independently had also investigated the possibility of self-focusing and self-trapping of light. In the meantime, it was also realized that self-focusing was the cause of many anomalies in the observation of stimulated Raman scattering in liquids (Shen and Shaham, 1965; Lallemand and Bloembergen, 1965; Hanchecorne and Mayer, 1965; Pilipetskii and Rustamov, 1965; Talanov, 1965; Kelley, 1965). Experiments (Chaio *et al.*, 1966; Brewer and Lifshitz, 1966; Brewer and Townes, 1967; Brewer *et al.*, 1968) showed that a self-focused beam usually turns into one or more small filaments. Each filament lasts for a few cm and has a diameter of a few μm which is approximately a constant, depending on the medium. The intensity of the filaments is in the 10^{10} W/cm^2 range and the light from the filament often shows a spectral broadening of as much as 100 cm^{-1} or more. Since then, the subject has

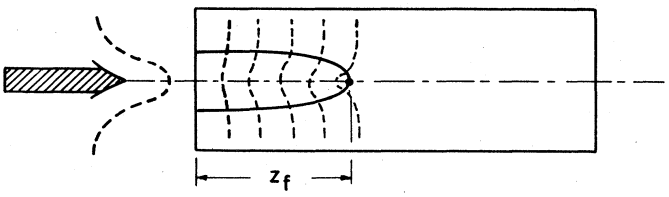

FIG. 8. Sketch showing the distortion of the wave front and self-focusing of a laser beam in a nonlinear medium.

attracted a great deal of attention. The solution of the problem, both theoretical and experimental, turned out to be more difficult than one had expected. Only after many slow steps of closely coupled theoretical and experimental advances are we now able to construct a more coherent picture of self-focusing and related phenomena. A number of review articles on the subject have already appeared in the literature (Akhmanov *et al.*, 1972; Svelto, 1974; Lugovoi and Prokhorov, 1974; Askar'yan, 1974; Shen, 1975). Here we shall only give a brief physical description based on our most recent understanding of the effect.

Physically, self-focusing may occur when the refractive index of the nonlinear medium increases with the beam intensity,

$$n = n_0 + \Delta n(|E|^2),$$

where $\Delta n(|E|^2)$ is the field-induced refractive index. The possible physical mechanisms responsible for Δn are libration, reorientation, and redistribution of molecules, electrostriction, deformation of electronic clouds, heating, etc. (see, for example, Akhmanov *et al.*, 1972; Svelto, 1974). Consider a laser beam with a Gaussian transverse profile propagating into the medium. The central part of the beam sees a larger refractive index than the edge and therefore propagates with a lower velocity. Consequently, as the beam traverses the medium, the original plane wave front gets more and more distorted, as shown in Fig. 8. Since the rays should propagate in a direction perpendicular to the wave front, the beam appears to focus by itself. A beam with a finite cross section will of course also diffract. Self-focusing occurs only if the self-focusing action is stronger than the diffracting action. Otherwise, the beam will still diffract, even though the diffraction should be weaker be cause of Δn. In particular, when self-focusing is just completely cancelled by diffraction over a long distance, the beam will then propagate without any change in its transverse profile. This is known as self-trapping (Chiao *et al.*, 1964; Askar'yan, 1962).

Since a high-intensity laser beam is usually necessary to induce a sufficiently large Δn for self-focusing, pulsed lasers are often used in the experiments. Two special cases are of interest. First, if the pulse width is much longer than the response time of Δn, the response of Δn to the laser intensity variation can be considered as instantaneous. We have the case of quasi-steady-state self-focusing. Second, if the pulse width is comparable with, or shorter than, the response time of Δn, the lagging part of the pulse will then see a Δn induced by the leading part. This gives rise to transient self-focusing. In the following, we shall consider the two cases separately.

Formally, both quasi-steady-state and transient self-focusing can be described by the nonlinear wave equation

$$\nabla^2 E + (\partial^2/c^2\partial t^2)[(n_0 + \Delta n)^2 E] = 0, \tag{6.1}$$

where Δn obeys an appropriate dynamic equation, depending on the physical mechanism responsible for Δn. For example, in liquids with strongly anisotropic molecules (Kerr liquids), Δn induced by a Q-switched laser pulse is mainly due to field-induced orientation of molecules and hence should obey the Debye relaxation equation. If the response of Δn to the field is instantaneous and the field is not very strong, we can often write $\Delta n = n_2|E|^2$ and neglect the higher-order dependence on $|E|^2$. The solution of Eq. (6.1) is unfortunately very difficult. No rigorous analytical solution is available (see, for example, Akhmanov *et al.*, 1967). Even a numerical solution for the quasi-steady-state case has not yet been completed throughout the focal region. Here we shall discuss mainly the qualitative aspect of the self-focusing solution.

Let us consider first the quasi-steady-state case with $\Delta n = n_2|E|^2$. This happens for example with nanosecond pulses in Kerr liquids which have relaxation times in the picosecond region. The results of computer calculations suggest (Kelley, 1965; Goldberg *et al.*, 1967; Marburger and Dawes, 1968; Dawes and Marburger, 1969) that a single-mode laser beam with sufficiently high power first propagates with little change in its profile and then suddenly self-focuses into a sharp focal spot, as shown in Fig. 8. The calculated self-focusing dynamics in the prefocusing region has in fact been verified quantitatively by experiments (McAllister *et al.*, 1968; Maier *et al.*, 1970). The focal spot should appear at the distance

$$z_f(t) = K/[\sqrt{P(\xi)} - \sqrt{P_0}], \tag{6.2}$$

where $\xi = t - z_f n_0/c$, P is the laser power, and K and P_0 are constants, depending on the characteristics of the beam and the medium.

Equation (6.2) shows that if P is a function of time, then the focal spot should appear to be moving along the axis. Experimentally, it is well known that self-focusing of a pulsed laser beam leads to intense filaments of light. For many years, the filaments were believed to be a manifestation of self-trapping of light (see, for example, Brewer *et al.*, 1968). We now know that they are actually tracks of moving focal spots (Lugovoi and Prokhorov, 1968; Loy and Shen, 1969). Given K and P_0 [which can be measured (Wang, 1966)] in Eq. (6.2), we can easily find the trajectory of the focal spot. This is shown in Fig. 9 for a nanosecond pulse. It is seen that, starting from the point D, the focal spot splits into two: one moves first backward and then forward, and the other moves forward with a velocity always larger than the light velocity. Loy and Shen (1970; 1971) have performed time-of-flight measurements on the focal spot and shown quantitatively that the prediction of Eq. (6.2) is indeed correct. Using a streak camera, Korobkin *et al.* (1970) has observed the backward moving focal spot. Dyshko *et al.* (1967) have predicted that, for $P > 2P_0$, nonlinear aberration in self-focusing can give rise to multiple foci along the axis.

The moving focus picture has also been successful in explaining the many observed anomalies connected with quasi-steady-state self-focusing in ordinary Kerr liquids. Thus the anomalously sharp threshold for stimulated Raman and Brillouin scattering is due to sharp self-focusing (Wang, 1966). The forward-backward asymmetry in stimulated Raman and Brillouin scattering is caused by asymmetry in the self-focusing dynamics (Maier *et al.*, 1966, 1969; Loy and Shen, 1973). The spectral broadening of light from a filament is the result of phase modulation acquired by the self-focused light in traversing the medium (Shen and Loy, 1971; Wong and Shen, 1972). However, there are also a number of problems on quasi-steady-state self-focusing left unsolved. The self-focusing dynamics in the focal region is still not understood. How the extremely intense self-focused light induces and interacts with other nonlinear optical effects and limits the size of the focal spot is still a mystery. How the self-focused light diffracts from the focal region is also not known.

We now consider the case of transient self-focusing. This happens for example with picosecond pulses in ordinary Kerr liquids. Because of the transient response, the physical picture of self-focusing is quite different from the quasi-steady-state case, although the experimental observations appear to be similar. Qualitatively, the leading edge of the pulse sees only small induced Δn and shows weak or no self-focusing, but it may affect strongly the self-focusing dynamics of the lagging part. As shown in Fig. 10, the very first part (section a in the figure) of the pulse sees little Δn and diffracts almost linearly as it propagates. The next part (section b in the figure) sees somewhat larger Δn and accordingly diffracts not as strongly. The induced Δn by the front part is then large enough to cause the lagging part (sections c–f in the figure) to self-focus. However, as the beam propagates on, it sees a gradually decreasing Δn because the front part has diffracted. As a result, self-focusing of the lagging part tends to be more gradual. If no other strong nonlinear effect cuts off the self-focusing action suddenly, diffraction from the focal region will also be gradual, leading to a long focus. Knowing how the various parts of the pulse propagate in the medium, we can find how the transverse profile of the pulse gets deformed during propagation. This is sketched in Fig. 10, where we assume there is a limiting diameter for the focus. It is seen that the pulse is quickly deformed into a horn shape. Then, because of the slow focusing and diffraction, the horn-shaped pulse appears to have reached a stable form and propagates on for many cm without appreciable change in its shape. This stable form of horn-shaped propagation is known as dynamic trapping (Alashkevich *et al.*, 1971; Shimizu, 1973; Wong and Shen, 1974). Obviously, the neck of the horn sweeping along the axis should again lead to an intense filament and the strong phase modulation acquired by the neck part could give rise to large spectral broadening. Both filament and spectral broadening are characteristics of picosecond transient self-focusing.

Theoretically, transient self-focusing is described by Eq. (6.1) coupled with the dynamic equation of Δn. In the case of Kerr liquids, the dynamic equation of Δn is the Debye relaxation equation. While no analytical solution of the coupled equations is available, numerical solutions from computer calculations have been obtained by a number of researchers (Fleck and Kelley, 1969; Carman and Fleck, 1972; Shimizu and Courtens, 1971; Shimizu, 1973). Their results have confirmed the above qualitative picture.

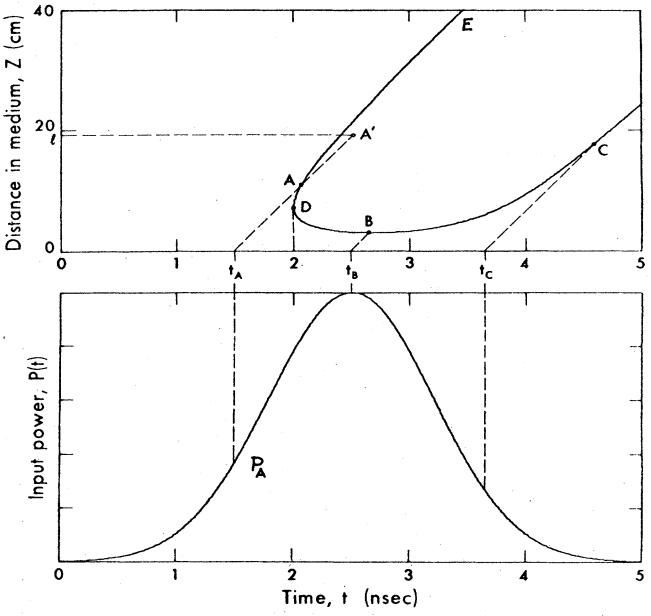

FIG. 9. Lower trace describes input power $P(t)$ as a function of time t. Peak power is 42.5 kW and the half-width at the $1/e$ point is 1 nsec. Upper trace, calculated from Eq. (6.2), describes the position of the focal spot as a function of time. Values of P_0 and K used are 8 kW and 11.6 cm-(kW)$^{1/2}$, respectively, which corresponds roughly to an input beam of 400 μm in diameter propagating in CS_2. The dotted lines, with the slope equal to the light velocity, indicate how light propagates in the medium along the z axis at various times (after M. M. T. Loy and Y. R. Shen, 1973).

Experimentally, quantitative measurements on transient self-focusing of picosecond pulses in Kerr liquids are difficult because of the limitations of picosecond technology. Recently, Wong and Shen (1973) have found that as a result of the pretransitional behavior, a liquid crystalline material can have a large field-induced Δn and a long relaxation time from ~10 nsec to ~1 μsec variable with temperature. Using such a material one can now study transient self-focusing with nanosecond Q-switched pulses, as has been done by Wong and Shen (1974). Their results show that the picture of dynamic trapping of Fig. 10 is indeed the correct description of transient self-focusing in Kerr liquids. They are also in semiquantitative agreement with the results of numerical calculations. By decreasing the relaxation time of the liquid crystalline material, it is also possible to study how transient self-focusing changes over to quasi-steady-state self-focusing. Work along this line is presently in progress.

In solids, electrostriction is the dominant mechanism for Δn. Therefore the dynamic equation for Δn is the driven acoustic wave equation and has a response time of ~10^{-7} sec for a beam diameter of several hundred μm. Then, even with nanosecond pulses, self-focusing in sol-

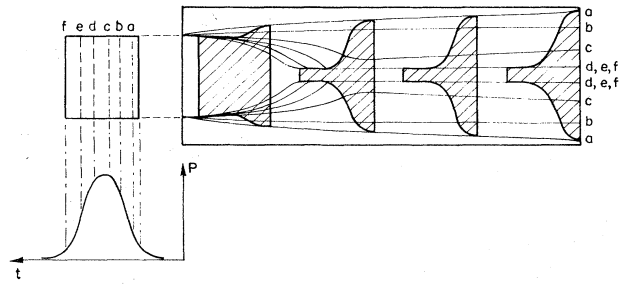

FIG. 10. Sketch showing transient self-focusing of a laser pulse in a Kerr liquid. Different parts (a, b, c, etc.) of the pulse focus and defocus along different ray paths. The pulse first gets deformed into a horn shape and then propagates on without much further change (after Wong and Shen, 1974).

ids is a transient phenomenon. We could use Fig. 10 to describe the phenomenon qualitatively, but there is an important difference here. In solids, a damage spot is created whenever the local light intensity has reached a threshold value. It then diffracts light strongly and prevents the trailing part of the pulse from self-focusing beyond the damage spot. We should therefore expect to find only a damage spot traveling along the axis in the backward direction. This has actually been observed by Zverev *et al.* (1969; 1970) and by Giuliano and Marburger (1971). The self-trapping model originally proposed by Chiao *et al.* (1964) can be refuted from the energy dissipation point of view. By solving Eq. (6.1) and the driven acoustic equation for Δn numerically, and assuming a threshold intensity for breakdown, Kerr (1972) has been able to calculate the damage trajectory in a solid for a given input laser pulse.

Self-focusing in solids is important in the design of high-power lasers. It is often the cause of damages in the laser rods. However, quantitative study of self-focusing in an amplifier medium has been rare (Fleck and Layne, 1973) and is certainly far from complete.

Self-focusing of laser pulses in gas has also been observed (Grischkowsky, 1970). Here the field-induced refractive index comes from the intensity-dependent anomalous dispersion of the refractive index due to electronic transitions (Javan and Kelley, 1966), and is well defined, even at very high intensity. Grischkowsky (1970) has observed clear self-focusing in potassium vapor. The minimum diameter of the self-focused beam was 50 μm. No other nonlinear optical effects appeared to be present to interfere with the self-focusing process. This is therefore a very attractive case for theoretical calculations. More recently, Bjorkholm and Ashkin (1974) have observed steady-state self-focusing in potassium vapor with a cw laser. They found that under suitable conditions the self-focused beam can funnel into a trapped filament. This is somewhat similar to the case of steady-state thermal self-focusing (Akhmanov and Sukhorukov, 1967; Dabby and Whinnery, 1968), where a positive Δn is induced by laser heating of the medium. In both cases, diffusion of energy out of the focal region transversely can act as an important balancing mechanism for the creation of stable trapped filament. With a pulsed dye laser, Bakhramor *et al.* (1975) have recently also observed self-focusing in potassium vapor under two-photon resonance excitation.

We can conclude by saying that we now have a fairly good understanding of the phenomenon of self-focusing in various media. Further progress in this field requires more quantitative results from both theoretical and experimental investigation.

VII. SOME THIRD-ORDER NONLINEAR OPTICAL EFFECTS IN CONDENSED MATTER

A few other interesting third-order nonlinear optical effects in condensed matter have been studied in recent years. In this section, we shall consider (a) four-wave mixing as a nonlinear spectroscopy technique and (b) nonlinear optical effects in liquid crystalline materials.

We have seen in Sec. V that stimulated Raman scattering can excite a material excitational wave and then coherent antiStokes scattering can be used to probe the excitational wave. In such an experiment, one can of course simply feed the Stokes in as an input beam instead of having it generated in the medium. When this is the case, we have actually a third-order optical mixing or four-wave mixing process in which the coherent anti-Stokes wave is generated as the fourth wave (Maker and Terhune, 1965). More generally, in four-wave mixing, we can have three input laser beams at ω_1, ω_2, and ω_3 interact in the medium and generate a fourth wave at $\omega_4 = |\pm\omega_1 \pm \omega_2 \pm \omega_3|$. We shall consider only the case where $|\omega_1 \pm \omega_2|$ is close to the resonance frequency ω_0 of a dispersionless material excitation. The underlying principle can of course be applied to other types of excitations.

From the general theory of optical mixing (see, for example, Bloembergen, 1965) it is easy to show that the fourth wave generated at phase matching over a distance z in the plane wave approximation is given by

$$|E(\omega_4)|^2 = (2\pi\omega_4^2/c^2k_{4z})^2 |\chi^{(3)}(\omega_4)|^2 \times |E(\omega_1)|^2 |E(\omega_2)|^2 |E(\omega_3)|^2 z^2 . \quad (7.1)$$

For $\omega_1 \pm \omega_2$ close to resonance, the third-order susceptibility $\chi^{(3)}(\omega_4)$ has the form (see, for example, Levenson and Bloembergen, 1974),

$$\chi^{(3)}(\omega_4) = \chi^{(3)}_{\rm NR}(\omega_4) + \chi^{(3)}_R(\omega_4) . \quad (7.2)$$

Assuming a Lorentzian line shape for the resonance, we can write the resonant part as

$$\chi^{(3)}_R(\omega_4) = A/(\omega_1 \pm \omega_2 - \omega_0 + i\Gamma) . \quad (7.3)$$

Both A and the nonresonant part $\chi^{(3)}_{\rm NR}(\omega_4)$ have negligible dispersion in the vicinity of ω_0. From Eqs. (7.1)–(7.3), one can see that the output $|E(\omega_4)|^2/|E(\omega_1)|^2|E(\omega_2)|^2 \times |E(\omega_3)|^2$ as a function of $\omega_1 \pm \omega_2$ goes through a maximum and a minimum corresponding to the maximum and the minimum of $|\chi^{(3)}(\omega_4)|$. The maximum and minimum occur at $\Delta\omega_+$ and $\Delta\omega_-$, respectively, with $\Delta\omega \equiv \omega_1 \pm \omega_2$ and

$$\Delta\omega_\pm = \omega_0 + \tfrac{1}{2}\{-A/\chi^{(3)}_{\rm NR} \pm ([A/\chi^{(3)}_{\rm NR}]^2 + 4\Gamma^2)^{1/2}\} . \quad (7.4)$$

This type of four-wave mixing experiment has been carried out in gases (DeMartini *et al.*, 1972; Lukasik and Ducuing, 1972; Regnier and Taran, 1973; Moya *et al.*, 1975), liquids and solids (Coffinet and De Martini, 1969; Wynne, 1972; Yablonovitch *et al.*, 1972; Leven-

son *et al.*, 1972; Akhmanov *et al.*, 1972; Levenson, 1974; Levenson and Bloembergen, 1974; Akhmanov *et al.*, 1974; Itzkan and Leonard, 1975) with $(\omega_1 - \omega_2)$ near a vibrational excitation, or with $(\omega_1 + \omega_2)$ near an excitonic transition (Kramer *et al.*, 1974). An example is shown in Fig. 11, where the resonant structure of $|\chi^{(3)}|$ is clearly displayed. From Eq. (7.4), we find

$$\Delta\omega_+ + \Delta\omega_- = 2\omega_0 - A/\chi^{(3)}_{NR},$$
$$[\Delta\omega_+ - \Delta\omega_-]^2 = (A/\chi^{(3)}_{NR})^2 + 4\Gamma^2. \quad (7.5)$$

In many cases one has $A/\chi^{(3)}_{NR} \gg \Gamma$, and hence the maximum of $|\chi^{(3)}|$ appears at $\Delta\omega_+ = \omega_0$. Knowing ω_0, we can then use Eq. (7.5) to deduce $A/\chi^{(3)}_{NR}$ and Γ from the measured values of $\Delta\omega_+ \pm \Delta\omega_-$. Normally, ω_0, A, and Γ can also be obtained from absorption or spontaneous scattering measurements. The four-wave mixing results can then yield an absolute value for $\chi^{(3)}_{NR}$. Such experiments, which involve only measurements of frequencies, have the advantage of being very accurate. However, we should note that in the more general cases where the resonance has a complex line shape or several resonant lines close together (Levenson and Bloembergen, 1974), the analysis often becomes far more complicated and less quantitative.

The nonlinear spectroscopic method discussed above has its output signal proportional to the product of intensities of the three input beams. Therefore the sensitivity of the method can be very high (Regnier and Taran, 1973; Begley *et al.*, 1974; Moya *et al.*, 1975) if the input laser intensities are high and the resonant line is narrow with $|\chi^{(3)}_R|_{max} > |\chi^{(3)}_{NR}|$. For example, with 1-MW input laser beams, roughly 1 W of coherent antiStokes signal from four-wave mixing can be generated via vibrational excitation of H_2 molecules in a 100 ppm H_2-in-N_2 mixture at atm. pressure (Regnier and Taran, 1973). As a comparison, a 1-MW laser beam can yield spontaneous Stokes emission of only $\sim 10^{-10}$ W per solid angle in the same focal volume. By monitoring the resonant structure in $|\chi^{(3)}|$, we can use the method to detect low-concentration substances in a gas mixture. Possible applications include study of gas mixtures in a flame, in a combustion engine, or in a supersonic jet flow (Regnier and Taran, 1973; Moya *et al.*, 1975), and monitoring of polluting substances in a smoke stack, automobile exhaust, or the atmosphere. We also note that the sensitivity of the method can be further improved by perhaps five to six orders of magnitude if we can let ω_1 or ω_2 approach a strong, narrow resonance.

Let us now change the subject to nonlinear optical effects in liquid crystalline materials. These materials are composed of long molecules with strong anisotropy. The molecular shapes and intermolecular forces tend to make the molecules align parallel to one another against thermal agitation. As a result, new phases, known as mesomorphic phases, appear between the phases of liquid and solid. In these new phases the molecules are more or less aligned with possible long-range structural order, but they may still retain certain degrees of translational and rotational freedom (see, for example, de Gennes, 1974). Of all the mesomorphic phases the nematic phase has the least molecular ordering: the molecules are aligned in one direction, but they are free to translate and to rotate about their long axes. The liquid crystalline system is analogous to a spin system with no spin polarity; each molecule here corresponds to a spin. Thus the liquid phase is equivalent to the paramagnetic phase, and the nematic phase to the ferromagnetic phase. In both phases, the material has an inversion symmetry, and hence no second-order nonlinear process is expected.

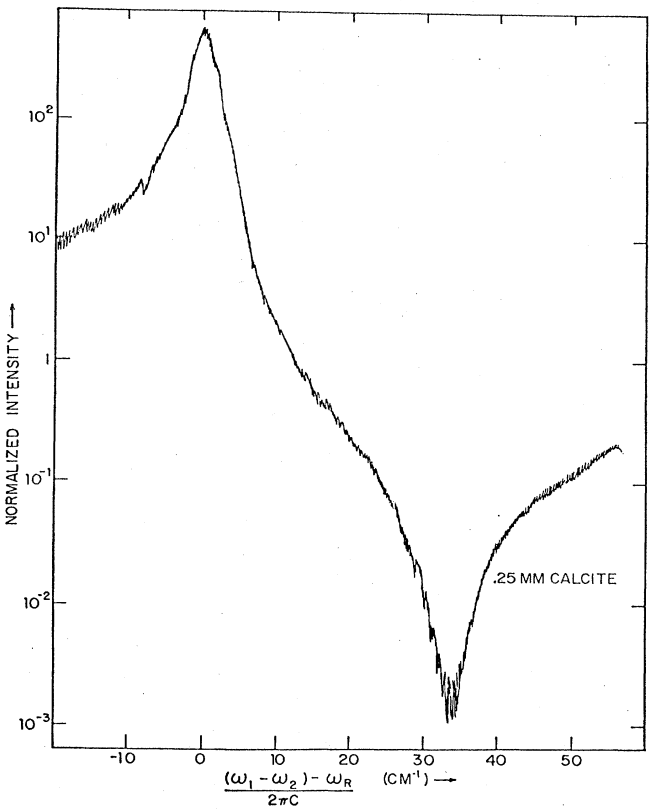

FIG. 11. Resonant structure of the 1088 cm^{-1} lattice mode of calcite in the antiStokes spectrum from the four-wave mixing spectroscopic technique. The polarizations of the waves were all perpendicular to the optical axis of calcite (after M. D. Levenson, 1974).

The third-order optical nonlinearity in such a medium is, however, quite large. Because of the strong molecular anisotropy, even an optical field can induce appreciable molecular alignment along the field. The induced alignment, and hence the induced birefringence, is proportional to $|E|^2$ or the optical intensity. In the liquid phase, this effect, known as the optical Kerr effect, is closely analogous to a paramagnetic spin system responding to an applied magnetic field. Here the light intensity plays the role of the magnetic field and the induced birefringence is equivalent to the induced magnetization. Thus we expect that the induced birefringence Δn in the liquid phase should obey the Curie law (Wong and Shen, 1973)

$$\Delta n = C|E|^2/(T - T^*) \quad (7.6)$$

for $T > T^*$, where C is a constant and T^* is the liquid-nematic transition temperature, assuming the transition

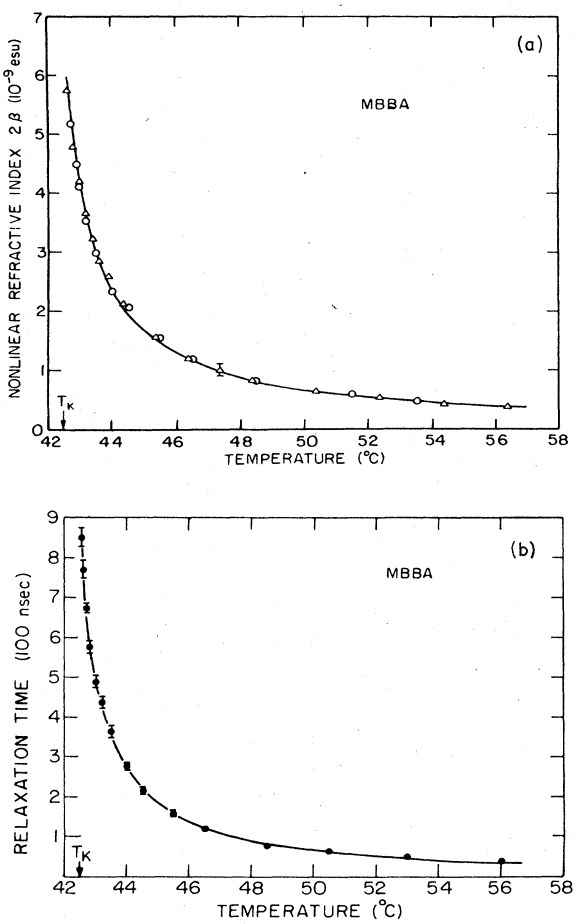

FIG. 12. (a) Nonlinear refractive index $2\beta(\Delta n = \pi\beta|E|^2/n)$ as a function of temperature for MBBA. △ (open triangles) are experimental data obtained from measurements of optical Kerr effect, ○ (open circles) are experimental data obtained from measurements of ellipse-rotation effect. The solid curve is the theoretical curve given by $(5.4\times10^{-9})/(T-T^*)$ esu with $T^* = 314.7$ °K. (b) Relaxation time τ of the order parameter as a function of temperature for MBBA. The solid curve is the theoretical curve. The dots are the experimental data points (after Wong and Shen, 1974).

is of second order. Experimental results on several liquid crystalline materials in the liquid phase agree well with Eq. (7.6) [see Fig. 12(a)] (Wong and Shen, 1973; 1974; Hanson, 1975). According to Eq. (7.6), Δn shows a critically divergent behavior as T approaches T^*. This is a result of a strong correlation between molecules near the transition temperature. However, the liquid-nematic transition is actually a first-order transition. It occurs at a temperature T_K, but for most nematic substances T_K happens to be only slightly above T^*. Consequently, Δn follows Eq. (7.6) quite closely until the first-order transition sets in at T_K. Because of this critical behavior, the induced Δn in liquid crystalline materials is usually very large. For example, the nematic substance MBBA at $T - T^* = 5$ °C has an optical Kerr constant almost 100 times larger than that of CS_2 (Wong and Shen, 1973; 1974b).

The induced alignment also shows a critical slowing down behavior, i.e., the relaxation time (or the response time) of Δn diverges as T approaches T^*. This is again analogous to the critical slowing down behavior of spin alignment in a paramagnetic system. The relaxation time τ takes the form (Wong and Shen, 1973; 1974b)

$$\tau = C'\nu/(T - T^*), \tag{7.7}$$

where C' is a constant and ν is a viscosity coefficient. As shown in Fig. 12(b) for a typical liquid crystalline material, Eq. (7.7) describes the experimental results very well. Presumably because of this critical behavior, τ for liquid crystalline materials is considerably longer than that for ordinary liquids. It varies with temperature over a wide range, typically from a few nsec near the boiling temperature to several hundred nsec near T_K. For comparison, τ for CS_2 is only 2 psec.

The large Δn and the long adjustable τ make the liquid crystalline materials particularly suitable for study of self-focusing (Wong and Shen, 1974; Rao and Jayaraman, 1973; 1974). As already mentioned in Sec. VI, experiments on self-focusing in MBBA have yielded the first quantitative information about the transient self-focusing phenomenon (Wong and Shen, 1974). As a result of self-focusing, stimulated Raman and Brillouin scattering can be generated in the focal region. Both stimulated Raman and stimulated Brillouin radiation from liquid crystalline materials have been observed (Wong and Shen, 1974; Rao and Aggarwal, 1971), but their relation with self-focusing has not yet been explored.

Another nonlinear optical effect of interest is the third-harmonic generation (or, more generally, sum-frequency generation) in cholesteric liquid crystals (Shelton and Shen, 1970; 1971; 1972). A cholesteric liquid crystal can be considered as a nematic liquid crystal twisted around an axis perpendicular to the direction of molecular alignment. The molecules form layers; in each layer the molecules are aligned parallel to the layer, but as the layer advances, the direction of alignment gradually rotates. As a result, the material has an overall helical structure. What we have, therefore, is a one-dimensional periodic structure with the period equal to one-half of the helical pitch p. It turns out that the pitch of a cholesteric liquid crystal can easily be varied from $\sim\pm0.2$ μ to several hundred microns by almost any external perturbation, such as the temperature.

A number of interesting optical properties of cholesteric liquid crystals result from this one-dimensional periodic structure. For example, optical Bragg reflection exists in such a medium. This leads to the brilliant color of some samples. Such a medium has a crystal momentum $G = 4\pi/p$ along the helical axis. Any integer of G can participate in the momentum (or wave-vector) conservation of wave mixing processes. In recent years much effort has been devoted to the development of solids with a superlattice (see, for example, Esaki, 1974; Cho, 1971), i.e., solids with a prescribed one-dimensional periodic structure. Novel transport properties are expected from a superlattice (Esaki and Chang, 1974). By adjusting the period to obtain an appropriate crystal momentum (2π/period), phase matching of optical sum-frequency generation is possible in a superlattice (Bloembergen and Sievers, 1970). Now, in a cholesteric liquid crystal, the one-dimensional structure is

given by nature. Moreover the period is easily adjustable. We therefore expect that phase matching of optical third-harmonic generation can be easily achieved in such a medium. At phase matching, the efficiency of third-harmonic generation is of course a maximum.

The phase-matching condition for third-harmonic generation can be written generally as (Shelton and Shen, 1972)

$$\pm k(\omega) \pm k(\omega) \pm k(\omega) = \pm k(3\omega) \pm mG\,, \tag{7.8}$$

where we assume all waves propagating along the helical axis, the + and − signs in front of the wave vectors k indicate forward and backward propagation respectively, and m is an integer. Knowing the dispersion of the refractive index of the medium, we can readily calculate from Eq. (7.8) the crystal momentum or the helical pitch necessary for phase matching. Experimentally, one can then vary the sample temperature to obtain the desired helical pitch. Figure 13 is an example, where all waves are propagating in the same direction and hence a small G or a large p is needed to compensate the mismatch between $k(3\omega)$ and $3k(\omega)$. It shows a good agreement between experiment and theory. Many other phase-matching cases with two fundamental beams propagating in opposite directions or with the fundamental and the third-harmonic beams in opposite directions have also been checked experimentally (Shelton and Shen, 1972). Equation (7.8) suggests that these processes are analogous to the umklapp processes of electrons and phonons in crystals. They have therefore been called "coherent optical umklapp processes." Phase-matched third-harmonic generation could be efficient if the medium is ordered over a long distance. Unfortunately, incoherent light scattering in liquid crystals is usually very strong. Also, it is difficult to obtain a single-domain sample with a thickness of more than 1 mm.

Nonlinear optics in liquid crystals is still at its beginning stage. We expect more studies of other nonlinear optical effects will be carried out in the near future.

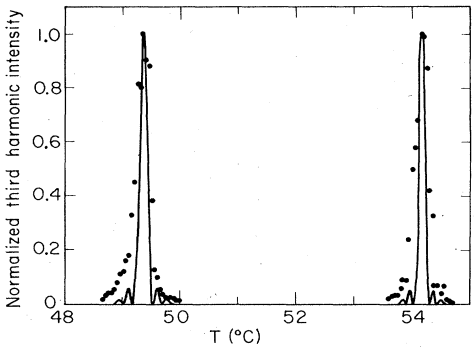

FIG. 13. Normalized third-harmonic intensity versus temperature near the phase-matching temperatures for the mixture of 1.75:1.00 by weight of cholesteryl chloride and cholesteryl myristate, in a cell 130 μm thick. The peak at the lower temperature (corresponding to left helical structure) is generated by right-circularly polarized fundamental waves and the one at the higher temperature (corresponding to right helical structure) by left-circularly polarized fundamental waves. The solid line is the theoretical phase-matching curve and the dots are experimental data points. The uncertainty in the experimental third-harmonic intensity is about 20% (after Shelton and Shen, 1970).

VIII. HIGH-RESOLUTION NONLINEAR OPTICAL SPECTROSCOPY

It is well known that, in general, both homogeneous and inhomogeneous broadening contribute to the width of an optical absorption or emission line, but inhomogeneous broadening usually dominates. This is particularly true for atoms or molecules in gases. The inhomogeneous Doppler linewidth can be several orders of magnitude larger than the homogeneous linewidth and limits the resolution of conventional spectroscopy. For higher resolution, we must find ways to overcome the obstacle of inhomogeneous broadening.

Soon after the invention of lasers, it was recognized that they could be used to circumvent the problem of inhomogeneous broadening in high-resolution spectroscopic work (Lamb, 1964; Szöke and Javan, 1963; McFarlane *et al.*, 1963). A highly monochromatic laser beam resonantly excites only a subset of atoms or molecules within the inhomogeneous linewidths. If the laser beam is intense, then a "hole is burned" in the inhomogeneous line due to saturation. This saturable absorption or "hole-burning" property has led to a number of interesting nonlinear spectroscopic techniques which are now being widely used in high-resolution spectroscopy of gases. Quite a few review articles already exist in the literature (see, for example, articles in books edited by Feld *et al.*, 1973; Brewer and Mooradian, 1974; Jacobs *et al.*, 1975; see also Hanach, 1973). Here we shall only briefly discuss the principles of the various techniques.

Consider first the Lamb dip effect (Lamb, 1964). A monochromatic traveling wave with frequency ω should interact most strongly with the group of atoms whose resonant frequency ω_0 and velocity component v along the propagation direction satisfy the relation (we consider only the first-order Doppler shift in this section)

$$|\omega(1 - v/c) - \omega_0| \lesssim \gamma\,,$$

where γ is the homogeneous half-width of the resonance. In the case of two oppositely traveling waves, there are two corresponding groups of atoms, with v in a narrow range of $\Delta v = 2\gamma c/\omega$ around $\pm|\omega - \omega_0|\, c/\omega$, respectively, interacting strongly with the waves. However, as ω approaches ω_0, these two velocity groups merge together. The atoms with nearly zero axial velocity can now interact simultaneously with both traveling waves. Therefore, if the field is sufficiently strong to cause saturation in the excitation, we expect to see an appreciable reduction in absorption or emission as ω approaches ω_0. In the lowest-order approximation, this reduction appears as a Lorentzian line with a half-width equal to the homogeneous halfwidth γ. The effect was first predicted by Lamb (1964) and observed by Szöke and Javan (1963), and by McFarlane *et al.* (1963). The narrow line is known as the Lamb dip in an amplifying medium or inverted Lamb dip in an absorbing medium. An example of the Lamb dip or saturation spectroscopy is shown in Fig. 14. With this technique, even the Lamb shift can now be observed by optical means (Hansch *et al.*, 1972). The technique has also been used to obtain a better value for

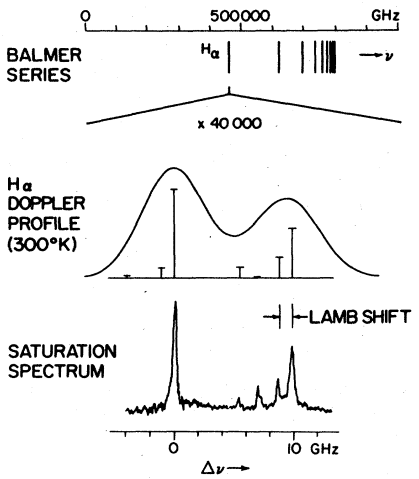

FIG. 14. Fine structure components of the red Balmer line of atomic hydrogen resolved from the Doppler profile by the saturation spectroscopic technique. Even the Lamb shift can be observed optically (after Hänsch *et al.*, 1972).

the Rydberg constant (Hansch *et al.*, 1974).

The Lamb dip, or nonlinear saturation spectroscopy, is now being widely used as a precision spectroscopic method. It has been used to measure isotope shifts, hyperfine splittings, fine structure due to molecular rotation, collisional broadening, etc. A homogeneous linewidth as narrow as 6 kHz can be measured, corresponding to an optical resolution higher than 10^{10} (Hall and Bordi, 1973). In the earlier years, the measurements were limited to transitions coincident with available discrete laser lines. This limitation has now been eliminated by the advent of tunable dye lasers (Hansch, 1973). As another application, the Lamb dip has been used effectively to achieve stable single-mode operation of gas lasers (see, for example, Hall, 1973).

Another high-resolution nonlinear spectroscopic technique based on a similar idea was proposed by Schlossberg and Javan (1966). Consider two closely spaced Doppler-broadened transitions which have resonant frequencies ω_{10} and ω_{20} and share a common energy level as shown in Fig. 15. If the system interacts with two oppositely traveling waves of frequency ω, we can easily show that when $|\omega - (\omega_{10}+\omega_{20})/2| \lesssim \gamma$, the two oppositely traveling waves interact simultaneously with the same group of atoms having an axial velocity $v \cong c(\omega_{20}-\omega_{10})/(\omega_{20}+\omega_{10})$. With sufficiently high field intensity, a Lamb-type dip would again show up at $\omega = (\omega_{10}+\omega_{20})/2$ in the

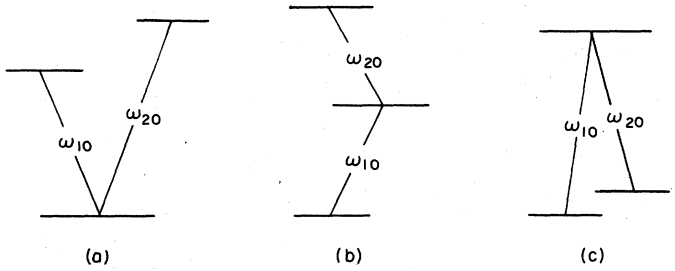

FIG. 15. Three possible configurations for two transitions sharing a common level (see Schlossberg and Javan, 1972).

Doppler-broadened spectrum. More generally, we can use a strong beam at ω_L to saturate one transition and a weak beam at ω to probe the saturation. When the two beams are propagating in the same direction, the Lamb-type dip appears at $\omega = \omega_L$. When the beams are in opposite directions, the dip appears at $\omega = \omega_L\omega_{10}/(2\omega_L - \omega_{20})$. This type of double-resonance saturation spectroscopy can be used to measure accurately the resonant frequencies of closely spaced transitions and their separations. The technique has recently been extended to two transitions with no common level but coupled by molecular collision (Brewer *et al.*, 1974).

There are a number of other high-resolution nonlinear spectroscopic techniques. In low-pressure gases, we can more conveniently detect the change in spontaneous emission than in absorption or amplification. We can, for example, observe the Lamb dip by monitoring the change in spontaneous emission induced by the nonlinear absorption (Feld and Javan, 1969). Laser-induced line narrowing in fluorescence has even been seen in solids (Szabo, 1970). Fluorescence from a set of coherently prepared excited states can also interfere and gives rise to a modulated fluorescence intensity. The modulation is known as "quantum beats" and can be used to measure small level splittings much smaller than the Doppler broadening (Gornik *et al.*, 1972; Haroche *et al.*, 1973).

More recently, with the help of tunable dye lasers, two-photon absorption has been proved to be a remarkable high-resolution spectroscopic technique to beat Doppler broadening. Consider two oppositely traveling waves of frequency ω in a gas medium with a resonant transition at ω_0. The condition for absorption of two oppositely propagating photons by an atom is

$$|\omega(1-v/c)+\omega(1+v/c)-\omega_0| \lesssim \gamma\,, \tag{8.1}$$

where v is the axial velocity of the atom. Equation (8.1) is independent of v, and therefore all atoms, regardless of their velocities, can be simultaneously excited by the two beams, while the absorption linewidth is given by the homogeneous width (Vasilenko *et al.*, 1970; Roberts and Fortson, 1973; Cagnac *et al.*, 1973). This has recently been demonstrated in alkali metal vapor by several research groups (Biraben *et al.*, 1974; Levenson and Bloembergen, 1974; Hansch *et al.*, 1974). Even with a low-power cw dye laser, the two-photon transitions can be observed with a large signal-to-noise ratio (see Fig. 16) (Hansch *et al.*, 1974; Bjorkholm and Liao, 1974). The technique has been used to study Zeeman splittings of a transition between two S states (Bloembergen *et al.*, 1974), the Stark splittings of $5s$ and $4d$ levels (Harvey *et al.*, 1974), and level shifts induced by two-photon transition (Liao and Bjorkholm, 1975) in sodium. It has also been used to study $1s$-$2s$ transition in atomic hydrogen (Hansch *et al.*, 1975) and fine structure in the vibrational transitions of molecules (Bischel *et al.*, 1975). Since all atoms in the medium are simultaneously excited as long as their resonant frequencies satisfy Eq. (8.1), this technique could be very useful for isotope separation (Kelley *et al.*, 1974).

In the above technique, if the two beams have different frequencies ω and ω', the Doppler broadening of the absorption line is not completely eliminated, but is signifi-

cantly reduced when the difference between ω and ω' is not large. This has the advantage that ω and ω' can now be varied independently. Either ω or ω' can be tuned to an intermediate state to resonantly enhance the two-photon absorption (Bjorkholm and Liao, 1974; Liao and Bjorkholm, 1975), or to probe the hyperfine structure of both the intermediate and the final states (Bjorkholm and Liao, 1974). Two-photon high-resolution spectroscopy is still in its infant stage. We can anticipate that in the near future the technique with its many variations will be most widely used in precision spectroscopic work (Bischel *et al.*, 1975; Hansch *et al.*, 1975).

IX. TRANSIENT COHERENT OPTICAL EFFECTS

The close analog between magnetic resonances and optical resonances has long been recognized. Feynman *et al.* (1957) have explicitly shown that any two-level system can be treated as a spin-$\frac{1}{2}$ system. In magnetic resonance, there are a number of well-known transient coherent phenomena (see, for example, Abragam, 1961). They are now being used routinely for relaxation studies in the radio and microwave range. These same phenomena are also expected in the optical region and have been the subjects of active research in recent years (see review articles by Courtens, 1972; Allen and Eberly, 1975).

When a circularly polarized quasimonochromatic field excites a transition in a material, the interaction of field with matter is usually dominated by contributions from the two levels involved in the transition. The material system can then be approximated by an effective two-level system. As shown by Feynman *et al.* (1957), the dynamic response of any two-level system to a rotating field can be described by the well-known Bloch equation for a spin-$\frac{1}{2}$ system,

$$\frac{\partial \langle \vec{p} \rangle}{\partial t} = -\frac{\gamma}{\hbar} \vec{E} \times \vec{p} - \frac{\hat{x}\langle p_x \rangle + \hat{y}\langle p_y \rangle}{T_2} - \frac{\langle p_z \rangle - \langle p_z \rangle_0}{T_1} \hat{z} . \qquad (9.1)$$

In this equation, γ is the dipole transition matrix element. $\langle \vec{p} \rangle$ is the average pseudodipole with $\langle p_x \rangle$ and $\langle p_y \rangle$ being the x and y components of the real induced dipole and $\langle p_z \rangle \equiv \gamma(\rho_{11} - \rho_{22})$, where ρ_{11} and ρ_{22} are the populations in the ground and excited states, respectively. $\vec{E}$ is a pseudofield with E_x and E_y being the x and y components of the applied field and $E_z \equiv -\hbar\omega_0/\gamma$, where ω_0 is the resonant frequency. T_1 and T_2 are longitudinal and transverse relaxation times, respectively. If the resonant transition shows inhomogeneous broadening then we should also average Eq. (9.1) over the distribution of resonant frequencies. Note that Eq. (9.1) reduces to the familiar form of Bloch equation for a magnetic system if we replace $\vec{P}$ by $\vec{M}$ and $\vec{E}$ by $\vec{H}$.

Equation (9.1) coupled with the Maxwell equations (or the em wave equation) essentially describes all the transient coherent optical effects in a two-level system. There is only one difference between a coherent optical phenomenon and its analog in magnetic resonance. The former deals with a propagating wave with a wavelength much smaller than the dimensions of the medium, while the latter deals with a standing wave with a wavelength comparable with or smaller than the dimension of the medium. Because of the wave propagation effect, however, rigorous solutions of transient coherent optical phenomena become much more difficult. Here we shall only discuss the various phenomena qualitatively. Usually it is more convenient to describe the Bloch equation in a coordinate system which rotates about $\hat{z}$ with the carrier frequency ω of the rotating (circularly polarized) field. In the rotating coordinates, the effective field acting on the pseudodipole is static,

$$\vec{E}_{\text{eff}} = \vec{\mathcal{E}} + (\hbar/\gamma)(\omega - \omega_0)\hat{z} , \qquad (9.2)$$

where $\vec{\mathcal{E}} = \hat{x}\mathcal{E}_x + \hat{y}\mathcal{E}_y$ is the amplitude of the applied field. The Bloch equation then describes the precession of the pseudodipole around $\vec{E}_{\text{eff}}$ with a frequency $\Omega = \gamma |E_{\text{eff}}|/\hbar$ (Fig. 17), subject to the initial condition and damping by the T_1 and T_2 relaxation processes.

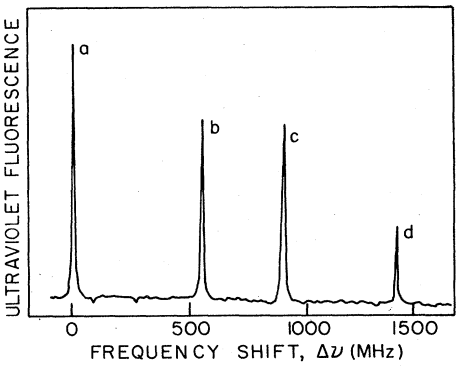

FIG. 16. Hyperfine structure of the $3S-4D$ transition in atomic Na resolved from the Doppler profile by the two-photon Doppler-free spectroscopic technique (after Hänsch *et al.*, 1974).

In the earlier years, the following coherent optical effects were experimentally discovered.

(1) *Optical nutation (Tang and Statz, 1968; Hocker and Tang, 1969).* This is an analog of transient nutation in magnetic resonance. As shown in Fig. 17, the pseudodipole $\langle \vec{p} \rangle$ is initially along $\hat{z}$. If a coherent radiation at resonance is suddenly switched on, then $\langle \vec{p} \rangle$ begins to precess around $-\vec{E}_{\text{eff}}$ perpendicular to $\hat{z}$ with a frequency $\Omega = \gamma |E_{\text{eff}}|/\hbar$. The up and down motion of $\langle \vec{p} \rangle$ corresponds to a sinusoidal oscillation in the population difference be-

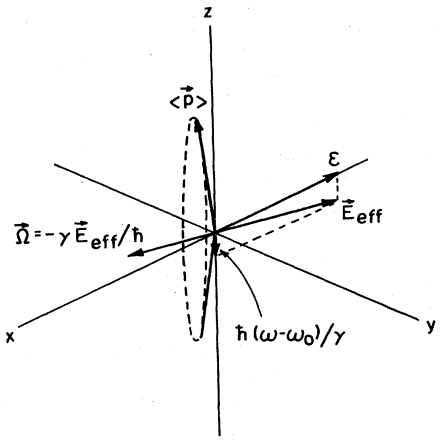

FIG. 17. Precession of a pseudo-dipole $\langle \vec{p} \rangle$ around the vector $\vec{\Omega} = -\gamma \vec{E}_{\text{eff}}/\hbar$ in a frame rotating about $\hat{z}$ with a frequency ω.

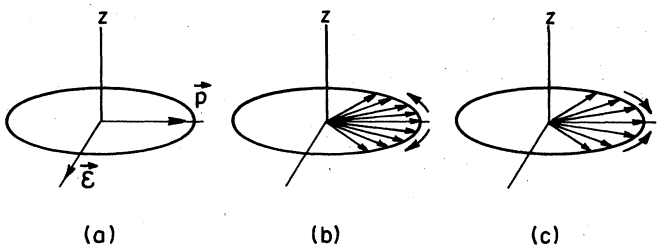

FIG. 18. Sketch of the pseudodipole assembly at various stages in the photon echo experiment. (a) Immediately after a $\pi/2$ pulse, all the dipoles are along the same direction perpendicular to $\hat{z}$ and $\vec{\mathcal{E}}$. (b) After the $\pi/2$ pulse, the dipoles start to fan out. (c) A π pulse is applied to flip the dipoles by 180° about $\vec{\mathcal{E}}$, and then the dipoles start to fan in.

tween the two levels. This oscillation reacts back on the propagating wave and results in an amplitude modulation of light. The modulation is finally damped out by relaxation. In order to see optical nutation, the precession frequency Ω must be of the order of or greater than, the transition linewidth.

(2) *Photon echoes (Kurnit et al., 1964; Abella et al., 1966; Abella, 1969).* This is an analog of spin echoes in magnetic resonance. It can be easily visualized with the help of Fig. 18. Application of the first resonant coherent pulse with $(\gamma/\hbar)\int_{-\infty}^{\infty}\mathcal{E}dt \sim \pi/2$ rotates the dipoles $\vec{p}$ from $\hat{z}$ by 90° about $\vec{\mathcal{E}}$. The dipoles then precess around $\hat{z}$ with a frequency ω_0. As a result of inhomogeneous broadening, different dipoles precess with slightly different ω_0, and hence fan out in the x-y plane. At a time τ after the first pulse, we apply a second resonant coherent pulse with $(\gamma/\hbar)\int_{-\infty}^{\infty}\mathcal{E}dt \sim \pi$. Each dipole is now rotated by 180° about $\vec{\mathcal{E}}$. After the pulse is over, the dipoles again precess around $\hat{z}$, but they now appear to "fan in." Thus, at a time τ after the second pulse, all the dipoles coalesce into one giant dipole which radiates to give a giant pulse in the prescribed direction. This is known as a photon echo. In order to observe photon echoes, the pulse widths and the time duration τ must be less than the relaxation times T_1 and T_2.

(3) *Self-induced transparency (McCall and Hahn, 1967; 1969).* This is a coherent wave propagation effect with no analog in magnetic resonance. Consider a resonant coherent pulse with $(\gamma/\hbar)\int_{-\infty}^{\infty}\mathcal{E}dt = 2n\pi$, where n is a positive integer. Therefore, all the dipoles simply precess around $\vec{\mathcal{E}}$ by $2n\pi$, and return to their original states at the end of the pulse. The resonant medium then absorbs no net energy from the pulse and looks transparent to the pulse. Actually, the medium first absorbs energy from the leading part of the pulse but later re-emits the energy to the lagging part of the pulse. During the process, it delays and reshapes the pulse, or breaks the pulse into n 2π pulses ($\gamma\int_{-\infty}^{\infty}\mathcal{E}dt = 2\pi\hbar$). More generally, for $(2n-1)\pi \leq (\gamma/\hbar)\int_{-\infty}^{\infty}\mathcal{E}dt \leq (2n+1)\pi$, the pulse is expected to get deformed into n 2π pulses in passing through the resonant medium. Again, self-induced transparency occurs when the pulse width is smaller than or comparable with the relaxation times. Relaxation causes some energy dissipation in the medium.

(4) *$n\pi$ pulse propagation.* Stimulated by the discovery of self-induced transparency, a number of researchers have studied other cases of coherent resonant pulse propagation, in particular 0π and π pulse propagation. The 0π pulse ($\int_{-\infty}^{\infty}\mathcal{E}dt = 0$) also returns the precessing dipoles to their original states at the end of the pulse and should therefore experience self-induced transparency (Lamb, 1967; 1971; Grieneisen *et al.*, 1972; Barnard, 1973; Salamo *et al.*, 1974; Diels and Hahn, 1975). It can be considered as formed by a $+2\pi$ pulse and a -2π pulse. Then, propagating in the resonant medium, it may break up into two pulses. There is, however, one possible 0π pulse shape which may not get disintegrated in the propagation (Lamb, 1969; 1971; Barnard, 1973). Such a pulse can be called a "bound state" of two 2π pulses. This has led to the speculation that stability of elementary particles may be explained by nonlinear fundamental interaction (Rubenstein, 1970).

In magnetic resonance, a π pulse inverts the population in a two-level system (Rabi, 1937). In the optical case, this is only true near the entrance of the medium, since propagation in the resonant absorbing medium tends to transform the π pulse into either 0 or 2π. This has actually been observed (Gibbs, 1973). The π pulse propagation in an amplifying medium has also been considered. It has been suggested that a π pulse in an amplifying medium has the same stability as a 2π pulse in an absorbing medium and can be used to explain the short pulses from a mode-locked laser (Fox and Smith, 1967). The coherent pulse propagation theory has been applied to traveling laser amplifiers (McCall and Hahn, 1970) and has been shown to agree well with the experimental results (Fox *et al.*, 1968; Frova *et al.*, 1969).

Both theory and experiment have been greatly extended and improved in the years subsequent to the initial discoveries of these effects. For example, photon echoes (Patel and Slusher, 1968) and self-induced transparency (Patel and Slusher, 1967; Gibbs and Slusher, 1970, 1972; Slusher and Gibbs, 1972; Slusher, 1974) have been studied in gases in quantitative detail and have been shown to agree with theory. Under self-induced transparency, giant Faraday rotation has been observed (Gibbs *et al.*, 1974). The effects of level degeneracy (Rhodes *et al.*, 1968; Gordon *et al.*, 1969; Rhodes and Szöke, 1969; Zembrod and Gruhl, 1971; Salamo *et al.*, 1974) and off-resonance frequency pulling (Diels and Hahn, 1973, 1975) have also been investigated.

A more recent advance in the experimental studies of coherent optical effects came in two ways. First, with the advent of tunable lasers, the experiments are no longer limited to only a few systems whose resonant frequencies accidentally match with available discrete laser frequencies. Second, it was realized by Brewer and Shoemaker (1971) that coherent pulse propagation in a resonant medium is equivalent to a cw wave propatation in a medium with its transition frequency suddenly shifted into or out of resonance by a pulse of external perturbation. The dc Stark effect is often used as a convenient way to shift the transition frequency. With these new techniques, the above mentioned coherent optical effects can be readily observed and measured to a high degree of accuracy. A number of other coherent optical effects described below have also been discovered as a consequence. All these effects have their counterparts in magnetic resonance.

(1) *Free induction decay (Brewer and Shoemaker,*

1971; 1972). Consider a cw laser beam with frequency ω propagating in a resonant medium. In the steady state, the pseudodipole $\langle p\rangle$ in Fig. 17 should be along $\vec{E}_{\rm eff}$. If the system is suddenly Stark-shifted out of resonance by $\Delta\omega$, then $\langle p\rangle$ will start to precess essentially around $\hat{z}$ with a frequency $\omega+\Delta\omega$, giving out radiation at $\omega+\Delta\omega$. This radiation dies away exponentially with a rate equal to the transition linewidth under the cw resonant excitation. Since the emission from this free induction decay is coherent, it can beat with the incoming cw wave and create a beat signal at $\Delta\omega$. Foster *et al.* (1975) have recently studied optical free induction decay in a degenerate system.

(2) *Adiabatic following*. The effective field $\vec{E}_{\rm eff}$ in Fig. 17 can be varied by varying either the frequency $\omega-\omega_0$ or the applied field strength $\mathcal{E}$. If the variation is sufficiently slow (in the adiabatic sense), then $\langle\vec{p}\rangle$ precessing around $-\vec{E}_{ff}$ follows $-\vec{E}_{\rm eff}$ and is nearly along $-\vec{E}_{\rm eff}$ all the time (see, for example, Abragam, 1961). This gives a good qualitative description of a number of near-resonant coherent pulse propagation phenomena (Grischkowsky *et al.*, 1973b). These include pulse delay (Grischkowsky, 1973), pulse reshaping and compression (Grischkowsky, 1974), self-steepening and self-phase modulation (Grischkowsky *et al.*, 1973a), self-focusing and defocusing (Grischkowsky, 1970; Grischkowsky and Armstrong, 1972), and dispersive amplitude modulation (Loy, 1975; Grischkowsky and Loy, 1975).

(3) *Adiabatic inversion*. By varying either ω or ω_0 such that $\vec{E}_{\rm eff}$ changes its direction slowly (or adiabatically) from $-\hat{z}$ to $+\hat{z}$, we can flip the dipole $\langle\vec{p}\rangle$. Physically, this means an inversion of population through adiabatic following. Observation of adiabatic inversion was first proposed and attempted by Treacy (1968; Treacy and DeMaria, 1969), but the results were rather inconclusive. Recently, using the Stark-shift technique to vary ω_0, Loy (1974) was able to demonstrate the effect unambiguously.

(4) *Superradiance*. As originally suggested by Dicke (1954), N "two-level" atoms with inverted population can establish correlation among themselves through interaction with the radiation field. Once the correlation is established, they form a giant dipole emitting radiation at a rate proportional to N^2, as opposed to the uncorrelated spontaneous emission rate proportional to N. This giant dipole emission is often called superradiance. From the classical point of view, this is not at all surprising. A system of N oscillating dipoles with phases correlated is expected to radiate at a rate proportional to N^2, for example, in the case of free induction decay. What is subtle in the superradiance problem is the question how the N atoms, originally uncorrelated (as manifested by the spontaneous emission rate proportional to N), establish correlation through interaction with radiation (Allen and Eberly, 1974). The transition from spontaneous emission to cooperative emission clearly needs a quantum description. Then it must also in some way be connected to the question of how stimulated emission evolves from spontaneous emission. The problem is probably academic, but it is still not clearly understood yet. The lack of a well-defined superradiant case isolated from other physical effects has generated a great deal of confusion in the field.

In the optical case, we have additional complications arising from wave propagation effects. For example, there is a limit on N since only atoms within the distance traveled by light in a superradiant time can be correlated (Arecchi and Courtens, 1970). There are also experimental difficulties in preparing a system with proper initial conditions for unambiguous observation of optical superradiance, in particular, transition from spontaneous to cooperative emission. Although many reports (Compaan and Abella, 1971; Shoemaker and Brewer, 1972; Skribanowitz *et al.*, 1973) have claimed the observation of some form of superradiance, a clean and more convincing experiment has yet to be performed.

There are also a number of other coherent optical effects reported in the literature. These include two-pulse optical nutation (Schmidt *et al.*, 1972), multipulse photon echoes (Schmidt *et al.*, 1972), coherent transient study of molecular collisions (Schmidt *et al.*, 1973; Berman *et al.*, 1975), coherent Raman beats (Shoemaker and Brewer, 1972; Brewer and Hahn, 1973), coherent transient birefringence in molecular vapor (Heritage *et al.*, 1975), two-photon self-induced transparency (Tan-no and Yokoto, 1972), and other two-photon coherent transient processes (Brewer and Hahn, 1975; Tan-no *et al.*, 1975).

Apparently, the field still has a great future. Compared with that in magnetic resonance, research on coherent optical effects is still in its early development stage. With the recent technical advances, studies of the more sophisticated coherent optical effects are now possible. For instance, the use of coherent pulses at two or more different frequencies in multiresonances with a multilevel system can lead to many interesting coherent optical phenomena.

Applications of transient coherent effects are mainly in the measurements of relaxation times of the excited states. Through the measured relaxation times, information about various interactions and external perturbations on relaxation can be deduced. Recently it has been proposed that adiabatic inversion can be used as an efficient method for isotope separation (Nebenzahl and Szöke, 1974).

X. NONLINEAR OPTICAL EFFECTS IN PLASMAS

Plasma is a highly nonlinear medium. Even in relatively dilute plasma, the nonlinear effects can easily be observed (see, for example, Tsytovich, 1970). Various nonlinear optical effects such as harmonic generation, parametric amplification, and stimulated light scattering were predicted almost a decade ago (see, for example, Kroll *et al.*, 1964; Dubois and Goldman, 1965; Bloembergen and Shen, 1965, Jha, 1965). More recently, because of its intimate relation with laser-induced fusion, nonlinear optics in plasmas has suddenly become a blooming field. A large number of theoretical and experimental papers have been written on the subject in the last three or four years. Here we have only space for a brief introduction to the field. For more details, we refer the reader to the conference proceedings (see, for example, proceedings edited by Schwarz and Hora, 1969, 1971, 1973). We shall limit our discussion to nonrelativistic gas plasmas.

Let us first discuss where the nonlinearities of plas-

mas come from. As usual, the response of a medium to an applied field is governed by the dynamic equations of the medium. Here, for electrons and ions which form a plasma, the dynamic equations are (1) the continuity equations and (2) the equations of motion for electrons and ions. We consider a two-component plasma (see, for example, Lee and Su, 1966) with an electron density $N_e(\vec{r}, t) = N_{e0} + n_e(\vec{r}, t)$ and an ion density $N_i(\vec{r}, t) = N_{i0} + n_i(\vec{r}, t)$, where N_{e0} and N_{i0} are the equilibrium densities. We shall always use the subindices e and i to indicate electrons and ions, respectively. For electrons, the continuity equation is

$$\frac{\partial n_e}{\partial t} + \nabla \cdot [N_e \vec{v}_e] + \nu_e n_e = 0 , \tag{10.1}$$

where $\vec{v}_e$ is the electron velocity, and ν_e is a phenomenological damping constant, depending on frequency. (Nonlinear damping is being neglected here.) The equation of motion is

$$\frac{\partial \vec{v}_e}{\partial t} + (\vec{v}_e \cdot \nabla)\vec{v}_e = -\frac{1}{M_e N_e}\left(\frac{\partial p_e}{\partial n_e}\right)\nabla n_e + \frac{q_e}{m_e}(\vec{E} + \frac{1}{c}\vec{v}_e \times \vec{B}) , \tag{10.2}$$

where M is the mass, q is the charge, p is the pressure, and E and B are, respectively, the electric and magnetic fields present in the plasma. In terms of the temperature T and the adiabatic exponent γ, we can write $(\partial p_e/\partial n_e) = \gamma_e KT$, where K is the Boltzmann constant. We also have a corresponding set of equations for ions by simply replacing the subindex e by i in Eqs. (10.1) and (10.2). The fields E and B are also connected with the densities and velocities through the Maxwell equations

$$\nabla \cdot \vec{E} = 4\pi[n_e q_e + n_i q_i] , \tag{10.3}$$

$$\nabla \times \vec{B} - \frac{1}{c}\frac{\partial E}{\partial t} = \frac{4\pi \vec{J}}{c} = (4\pi/c)(N_e q_e \vec{v}_e + N_i q_i \vec{v}_i) . \tag{10.4}$$

The above equations show that the nonlinearities of a plasma come through the electric force and the Lorentz force on electrons in Eq. (10.2). The corresponding forces on ions are often negligible because of their heavy mass. This can be seen more clearly from the iterative solution of the equations. We expand the variables n, $\vec{v}$, $\vec{E}$, and $\vec{B}$ into series of ascending order, e.g., $n = n_1 + n_2 + \cdots$, etc. For the purpose of illustration, we neglect in Eq. (10.2) the $(\partial p/\partial n)$ term which is responsible for the dispersion of plasma oscillation. Then, from Eq. (10.2), we find first $v_{e1} \propto q_e E_1/m_e$, then $v_{e2} \propto E_1 E_1$ through $(\vec{v}_{e1} \cdot \nabla)\vec{v}_{e1}$ and $q_e \vec{v}_{e1} \times \vec{B}_1/m_e c$, etc. From Eq. (10.1), we have $n_{e1} \propto v_{e1} \propto E_1$, $n_{e2} \propto n_{e1} v_{e1} \propto E_1 E_1$, etc. The response of ions is coupled to that of electrons mainly through interaction with the field via Eq. (10.3).

The above nonlinear responses of electrons and ions can then give rise to many nonlinear optical effects. Let us first consider optical second-harmonic generation in a plasma. At optical frequencies, the response of ions is negligible because of their heavy mass. Then with $\{E_1, B_1\} \propto \exp(-i\omega t)$, we can easily show from Eqs. (10.1) and (10.2) that the second-order current density at 2ω is given by (Bloembergen *et al.*, 1968; Rudnick and Stern, 1971) (assume $\partial p/\partial n = 0$ again)

$$\vec{J}^{(2)}(2\omega) = N_{e0}\vec{v}_{e2}(2\omega) + n_{e1}(\omega)\vec{v}_{e1}(\omega) = \frac{iN_{e0}q_e^2}{2\omega^3 m_e^2}[(\vec{E}_1 \cdot \nabla)\vec{E}_1 + i\omega \vec{E}_1 \times \vec{B}_1] + \frac{iq_e^2}{m_e^2\omega^3}[\nabla \cdot (N_{e0}\vec{E}_1)]\vec{E}_1 . \tag{10.5}$$

It can also be written as

$$\vec{J}^{(2)}(2\omega) = \frac{iq_e^2}{m_e^2\omega^3}\left\{\tfrac{1}{4}N_{e0}\nabla(\vec{E}_1 \cdot \vec{E}_1) + \frac{(\nabla N_{e0} \cdot \vec{E}_1)\vec{E}_1}{1 - \omega_e^2/\omega^2}\right\} , \tag{10.6}$$

where $\omega_e^2 = 4\pi N_{e0} q_e^2/m_e$. This current density is the nonlinear source responsible for the second-harmonic generation. The expression of $\vec{J}^{(2)}(2\omega)$ can also be rearranged into an electric quadrupole part and a magnetic dipole part. No dipole term appears in $\vec{J}^{(2)}(2\omega)$ because of inversion symmetry. We note that in a uniform plasma ($\nabla N_{e0} = 0$), only the magnetic dipole part ($\vec{E}_1 \times \vec{B}_1$ term) can contribute to $\vec{J}^{(2)}(2\omega)$ in the bulk, while the electric quadrupole part often dominates at the surface (due to discontinuity in $\vec{E}_1$ or in N_{e0}). Then, since $\vec{E}_1 \times \vec{B}_1$ is a longitudinal component, no second-harmonic generation is possible in the bulk of a uniform plasma. In a nonuniform plasma, however, the ∇N_{e0} term in $\vec{J}^{(2)}(2\omega)$ can be effective for second-harmonic generation in the bulk. As seen in Eq. (10.6), this is more so when ω approaches the electron plasma frequency ω_e.

Experimentally, optical second-harmonic generation has been observed in reflection from metal surfaces (Brown *et al.*, 1965; Bloembergen *et al.*, 1968). The nonlinearity is believed to be due to electric quadrupole contribution at the surface from the electron plasma (Bloembergen *et al.*, 1968). Second-harmonic radiation has also been detected in the reflected light from a laser-induced plasma (Bobin *et al.*, 1973; Lee *et al.*, 1974; Eidmann and Sigel, 1975; Baldis *et al.*, 1975). In this case, the plasma was created by focusing a high-energy laser pulse on a solid target. It was an expanding plasma and therefore was extremely nonuniform. The second harmonics could then be generated in the bulk of the plasma. Quantitative analysis for such a case is difficult unless the laser-induced plasma can be well described.

There are a number of other important nonlinear optical effects in gas plasmas: Stimulated Raman scattering (SRS) arises from light scattering by electron plasma wave (optical plasma mode) or can be described equivalently as a result of parametric coupling between the incoming pump, the scattered Stokes, and the electron plasma waves (see, for example, Dubois and Goldman, 1965; Bloembergen and Shen, 1966). Stimulated Brillouin scattering is a similar process with the electron plasma wave replaced by ion-acoustic plasma wave (acoustic plasma mode) (Lee and Su, 1966). Parametric instability can in general result from parametric coupling between a pump beam and two or more plasma waves (see, for example, Solin, 1965; Nishikawa, 1968; Bobin *et al.*, 1973). These effects, all due to parametric coupling between waves, can be considered as special cases of the general parametric amplification process. Therefore, usual formalism for parametric amplification (see, for example, Bloembergen, 1965) is also valid here if we can only write down the plasma wave equations.

The plasma wave equations can be easily obtained from

Eqs. (10.1)–(10.3) and similar equations for ions (see, for example, Lee and Su, 1965; Kidder, 1971). For the optical modes, we can neglect the ionic response. Then the plasma wave equation is

$$\left[\frac{\partial^2}{\partial t^2} - \frac{1}{m_e}\left(\frac{\partial p_e}{\partial n_e}\right)\nabla^2 + \nu_e \frac{\partial}{\partial t}\right] n_e = \nabla \cdot \vec{F}\,, \tag{10.7}$$

where

$$\vec{F} = \left(\frac{q_e}{m_e}\right) n_e \vec{E} + N_e(\vec{v}_e \cdot \nabla)\vec{v}_e - \vec{v}_e \frac{\partial n_e}{\partial t} + N_e\left(\frac{q_e}{m_e c}\right)(\vec{v}_e \times \vec{B})\,. \tag{10.8}$$

In a uniform plasma, we have to the second order

$$\nabla \cdot \vec{F} = N_{e0} q_e (\vec{v}_{e1} \times \vec{B}_1)/m_e c\,. \tag{10.9}$$

For the acoustic modes, we anticipate approximate charge neutrality $n_e q_e + n_i q_i \simeq$ at all time. The corresponding plasma wave equation is

$$\left[\frac{\partial^2}{\partial t^2} - V_a^2 \nabla^2 + \nu_a \frac{\partial}{\partial t}\right] n_e = \left|\frac{m_e q_i}{m_i q_e}\right| \nabla \cdot \vec{F}\,, \tag{10.10}$$

where

$$V_a^2 = \frac{1}{m_i}\left[\left(\frac{\partial p_i}{\partial n_i}\right) + \left|\frac{q_i}{q_e}\right|\left(\frac{\partial p_e}{\partial n_e}\right)\right],$$

$$\nu_a = \nu_i + |m_e q_i / m_i q_e|\,\nu_e\,.$$

Equations (10.7) and (10.10) together with the optical wave equation

$$\nabla \times (\nabla \times \vec{E}) + \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\epsilon \vec{E} = -\frac{4\pi}{c}\frac{\partial}{\partial t}\vec{J}^{(2)} \tag{10.11}$$

can now be used to describe parametric processes in a plasma.

Consider first SRS. We have $\vec{E} = \vec{\mathcal{E}}_l \exp(i\vec{k}_l \cdot \vec{r} - i\omega_l t) + \vec{\mathcal{E}}_s \exp(i\vec{k}_s \cdot \vec{r} - i\omega_s t)$. Equation (10.11) can be decomposed into two equations, one for $\vec{E}(\omega_l)$ and one for $\vec{E}(\omega_s)$. The current densities are $\vec{J}^{(2)}(\omega_l) = i(q_e/m_e\omega_s) n_e(\omega_l - \omega_s) \times \vec{E}(\omega_s)$ and $\vec{J}^{(2)}(\omega_s) = i(q_e/m_e\omega_l) n_e^*(\omega_l - \omega_s)\vec{E}(\omega_l)$. Assume a uniform plasma with $\vec{E}(\omega_l)$ and $\vec{E}(\omega_s)$ polarized along the same direction. The driving term in Eq. (10.7) for $n_e(\omega_l - \omega_s)$ becomes $\nabla \cdot \vec{F} = -N_{e0}|\vec{k}_l - \vec{k}_s|^2 q_e^2 E(\omega_l) E^*(\omega_s)/m_e^2 \omega_l \omega_s$ in the second-order approximation. Then, if the depletion of the pump field at ω_l can be neglected and the dispersion of the plasma wave is sufficiently small, we can readily solve the coupled equations for $E(\omega_s)$ and $n_e(\omega_l - \omega_s)$. The solution shows that the Stokes intensity $|E(\omega_s)|^2$ grows exponentially with a maximum gain coefficient (Kidder, 1971) $G = 4\pi N_{e0} q_e^4 (k_l + k_s)^2 \epsilon^{1/2}(\omega_l)|E(\omega_l)|^2/m_e^3 c^3 k_l k_s \omega_l \omega_e \nu_e$ which appears when the Stokes scattering is in the backward direction and $(\omega_l - \omega_s)$ is equal to the electron plasma frequency, $\omega_{pe} = [\omega_e^2 + V_e^2(k_l + k_s^2)]^{1/2}$. For a weakly damped plasma with $\omega_e/\nu_e \sim 100$, the above result predicts a strong Stokes backscattering from the focal region of a 1 GW laser beam. Similar to SRS in other media, a more general treatment would also predict the generation of Stokes and antiStokes radiation of many orders in a plasma. Extensive theoretical calculations for SRS under various conditions (such as plasma with a density gradient and special boundary conditions) have been carried out (Forslund *et al.*, 1973; Galeev *et al.*, 1973; Klein *et al.*, 1973; Biskamp and Welter, 1975).

No observation of SRS in plasmas has yet been reported. A probable reason is that parametric instability normally has a lower threshold. Stimulated Brillouin scattering in laser-induced plasmas, however, has actually been observed when a laser beam of ~10 GW or more is focused on a solid target (Goldman *et al.*, 1973; Yamanaka *et al.*, 1974; Ripin *et al.*, 1974). The process is presumably responsible for the intensity-dependent reflection from the target. The theory of stimulated Brillouin scattering is essentially the same as that of SRS with the electron plasma wave replaced by the ion-acoustic plasma wave.

In stimulated Raman and Brillouin scattering, part of the incoming energy is being used to excite the plasma oscillations, which are then dissipated into heat. This therefore provides a means to heat a plasma with laser energy. In order to be more efficient, one can use two input laser beams, one at ω_l and one at ω_s with $\omega_l - \omega_s$ equal to the plasma frequency. The heating efficiencies, with and without cascade generation of higher-order Stokes radiation for both homogeneous and inhomogeneous plasmas, have been estimated (Cohen *et al.*, 1972; Rosenbluth and Liu, 1972; Kaufman *et al.*, 1973). If higher-order nonlinearities are taken into account, then, for example, the driving force $\nabla \cdot \vec{F}$ in Eq. (10.7) can have a component proportional to $n_e^* E(\omega_l) E^*(\omega_s)$, and hence the plasma oscillation can be excited by two beams with $\omega_l - \omega_s$ equal to twice the plasma frequency (Rosenbluth and Liu, 1972). Similarly, the plasma oscillation can also be excited when $\omega_l - \omega_s$ is equal to subharmonics of the plasma frequency (Fuchs *et al.*, 1973). Heating of plasma with ω_l and ω_s near resonance with the optical mode and $\omega_l - \omega_s$ at resonance with the acoustic mode has also been considered.

However, the most efficient way of heating the plasma is probably by parametric instability. In this parametric process, we have a pump field $\vec{E} = \vec{E}(\omega_l)$ and two plasma waves $n_e(\omega_1)$ and $n_e(\omega_2)$ which can be both optical or one optical and one acoustic, where $\omega_l = \omega_1 + \omega_2$. If $E(\omega_l)$ is sufficiently high, we again expect to see rapid growth of $n_e(\omega_1)$ and $n_e(\omega_2)$ at the plasma frequencies due to parametric excitation (Silin, 1965; Nishikawa, 1968). The plasma waves are then dissipated into heat. Heating due to parametric instability in a plasma pumped by microwave has already been observed (Porkolab *et al.*, 1972). In a laser-induced plasma, observation of parametric instability has also been reported (Bobin *et al.*, 1973; Yamanaka *et al.*, 1974; Lee *et al.*, 1974). Such a plasma is of course extremely inhomogeneous and in fact varying with time. Rosenbluth (1972) has treated parametric instability in an inhomogeneous plasma theoretically. Experiments on laser-induced plasma showed that reflected light peaked at $2\omega_l$, $3\omega_l/2$, and ω_l. The subharmonic lines can be explained as follows. The pump field can parametrically excite two electron plasma waves, both with frequency $\omega_{pe} = \omega_l/2$. At the same time, the plasma waves can mix with the pump light to produce radiation at $\omega_l \pm \omega_l/2$.

When third-order nonlinear response is considered, one can easily show that $\vec{J}^{(3)}(\omega) \propto |E(\omega)|^2 E(\omega)$, or the refractive index takes the form $n = n_0 + n_2|E(\omega)|^2$ with $n_2 > 0$. Kidder (1971) and Max *et al.* (1974) have also considered the relativistic mechanism for the nonlinear refractive index. Since $n_2 > 0$, both self-focusing and self-phase-

modulation can occur in a plasma. They have been seen in plasmas created by laser breakdown in gases (Korobkin and Alcock, 1968; Alcock *et al.*, 1969; Alcock *et al.*, 1970; Yablonovitch, 1974; Yamanaka *et al.*, 1975). However, it is likely that the observed self-focusing is actually due to plasma density gradient rather than optical nonlinearity in plasma (Johnson and Chu, 1974). Self-focusing and self-phase-modulation of light in a relativistic plasma have recently been considered by Max *et al.*, (1974).

In conclusion, we should note that the experimental situation for nonlinear optical measurements in plasmas is usually very complicated. For example, the variation of the plasma density and composition in space and time is often difficult to describe quantitatively. This is particularly true for a laser-induced plasma. Theoretical calculations, on the other hand, always use many simplifying approximations. Interpretations of experimental results are therefore at best qualitative. Advances in the field would require better defined experiments and more realistic calculations.

XI. NONLINEAR OPTICAL EFFECTS IN OPTICAL WAVEGUIDES

Recently, integrated optics has emerged as an immensely active field in quantum electronics because of its technological importance. In the course of its development, a question naturally arose on how nonlinear optical effects would behave in an optical waveguide (see, for example, Tien, 1971; Andrews, 1971; Zolotov *et al.*, 1974). A number of advantages in having nonlinear optical effects in optical waveguides are perhaps intuitively obvious. First, a laser beam can be focused into an optical waveguide and remain trapped in the waveguide over a long distance, whereas a focused beam in a bulk material diffracts readily from the focal spot. Second, phase matching in a waveguide can be achieved by varying the waveguide structure which determines the propagation characteristics of the guided waves. Third, besides phase matching, nonlinear interaction of the guided waves can also be varied by varying the waveguide structure. We shall use second-harmonic generation to illustrate the last two points more fully.

Second-harmonic generation is the only guided nonlinear optical effect which has been studied in great detail. Consider a thin-film waveguide shown in Fig. 19. From the theory of dielectric waveguides, we have for a monochromatic propagating waveguide mode,

$$E = \mathcal{E}(x, y) \exp[i\beta z - i\omega t] . \tag{11.1}$$

The expressions of $\mathcal{E}(x, y)$ and $\beta(\omega)$ are complicated but can easily be derived (see, for example, Burns and Andrews, 1972; Conwell, 1973). Both depend on the mode order, field polarization (TE or TM), and waveguide structure (waveguide width W and refractive indices n_0, n_1, and n_2 of the three sections in Fig. 19). If both the fundamental and the second-harmonic waves are in the form of guided modes, then the phase matching condition is satisfied when

$$2\beta(\omega) = \beta(2\omega) . \tag{11.2}$$

Without going into detail, one can already see that, for a given ω, the above equation can possibly be satisfied by adjusting either W or one of the n's. The nonlinear polarization at 2ω is of course also responsible for the second-harmonic generation. Since it is appreciable only in media without inversion symmetry, we should expect second-harmonic generation to be concentrated in those regions of the waveguide where the materials have no inversion center and $|\mathcal{E}(x, y, \omega)|^2$ is strong. The above consideration has led to a variety of designs for phase-matched second-harmonic generation in optical waveguides.

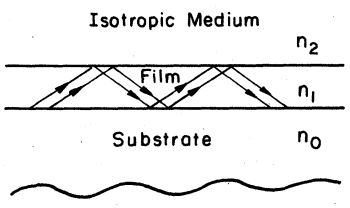

FIG. 19. Structure of an optical thin-film waveguide. The refractive indices of the three layers are n_0, n_1, and n_2, respectively, with $n_1 > n_0$, n_2.

Phase-matched second-harmonic generation has been observed in optical waveguides of the following structure: (1) a thin nonlinear crystalline wafer in air (Anderson and Boyd, 1971); (2) a thin film of glass (Suematsu *et al.*, 1973, 1974), or TiO_2 (Burns and Lee, 1974), or Al_2O_3 (Chen *et al.*, 1974) coated on a nonlinear substrate in air or in liquid (Burns and Lee, 1974); (3) an imperfectly oriented nonlinear polycrystalline film on a glass or fused quartz substrate (Ito *et al.*, 1974; Zemon *et al.*, 1972); (4) a double-heterostructure waveguide (van der Ziel *et al.*, 1974). With a laser beam of 100 W peak power, a second-harmonic output of 10 mW peak power in the visible can be obtained. Even cw harmonic generation in the uv has been observed with an input power of 0.5 W (Chen *et al.*, 1974).

There are, however, some serious difficulties which have so far prevented optical waveguides from being used as efficient nonlinear optical devices. First, if the waveguide width W is not a constant, the phase-matching condition of Eq. (11.2) cannot be satisfied in the entire waveguide. Detailed calculation would show that in order to have $\int_0^l |2\beta(\omega) - \beta(2\omega)|\, dz < \pi$ for $l > 1$ mm, one usually cannot allow W to vary more than a few percent (Tien, 1971). It is possible to make the phase-matching condition less sensitive to W by immersing the film-on-substrate structure in a liquid and adjusting the refractive index of the liquid properly (Burns and Anderson, 1973; Burns and Lee, 1974). Second, surface scattering, because of the surface imperfection, greatly enhances the loss, so that the propagation length in a waveguide is often limited to a few mm (Burns and Lee, 1974). Third, a high-power laser beam may damage the waveguide (Anderson and Boyd, 1971; Zemon *et al.*, 1972). These technological difficulties are perhaps also the reasons why parametric amplification has not yet been observed in optical waveguides.

In the case where the laser beam propagating in the waveguide induces a nonlinear polarization in the substrate, the second-harmonic radiation can also be generated as a freely propagating wave in the substrate. Here, phase matching between guided and freely propagating waves requires only the wave vector components parallel to the thin-film boundary to be matched (Szöke, 1964; Sacchi *et al.*, 1968; Tien *et al.*, 1970). For a

second-harmonic wave emitting at an angle α away from the film, the phase-matching condition is

$$2\beta(\omega) = k_0(2\omega)\cos\alpha\,, \tag{11.3}$$

where $k_0(2\omega) = 2\omega n_0(2\omega)/c$ is the second-harmonic wave vector in the substrate. Clearly, Eq. (11.3) can be satisfied as long as $k_0(2\omega) > 2\beta(\omega)$. Physically, this means that the phase velocity of the nonlinear polarization is larger than the light velocity in the substrate. This is therefore a close analog of the Cerenkov radiation. Observations of second-harmonic Cerenkov radiation from thin-film waveguides have been reported (Tien *et al.*, 1970; Chen *et al.*, 1974). Such a process does not depend critically on the small variation in the waveguide width, since Eq. (11.3) can always be satisfied with a slightly different emission angle α. Because of this noncritical dependence, the observed second-harmonic generation by Cerenkov radiation was actually more efficient than the phase-matched second-harmonic generation in the waveguide (Chen *et al.*, 1974).

Besides second-harmonic generation, the only other second-order nonlinear optical effect which has been observed in waveguides is the far-infrared difference-frequency generation. Because of the longer wavelength, a waveguide in the far infrared is much easier to construct. With two CO_2 lasers as the pump source, cw far-infrared generation in a GaAs waveguide has already been achieved (Thompson and Coleman, 1974).

Observations of third-order nonlinear optical effects in waveguides have also been reported. In this case, the experiments have so far been restricted to cylindrical waveguides with diameters appreciably larger than the wavelength. The propagating wave in the waveguide has often a multimode structure. The waveguide here is mainly for concentrating the laser beam in a medium over a long distance so that third-order nonlinear effects can build up to a high level despite the weak nonlinearity.

Ippen (1970) first demonstrated that quasi-cw Raman oscillation in CS_2 can be achieved with a pump power of less than 5 W if a liquid-core optical waveguide is used in a cavity. Later, stimulated Raman gain and Raman oscillation were also observed in glass optical waveguides, even though the Raman cross section of glass was quite small (Stolen *et al.*, 1972; Stolen and Ippen, 1973). More recently, cw Raman amplification was obtained in a benzene-filled liquid-core fused silica fiber of 5 m long with an input laser power less than 100 mW (Stone, 1975). The efficiency was higher than 20%. Phase-matched four-wave mixing and stimulated anti-Stokes radiation has also been seen in silica fibers (Stolen *et al.*, 1974; Stolen, 1975). Besides stimulated Raman scattering, optical Kerr effect (Stolen and Ashkin, 1973) and self-phase modulation (Ippen *et al.*, 1974) of light have also been observed in optical waveguides. Phase-matched second-harmonic generation in a nitrobenzene-filled waveguide has also been observed by using a periodic dc field to modulate the nonlinear susceptibility (Levine *et al.*, 1975).

Many other nonlinear optical effects in optical waveguides have yet to be investigated. The rate of progress in this field would strongly depend on the advances in the optical waveguide technology.

XII. MULTIPHOTON IONIZATION AND OPTICAL BREAKDOWN

There are a number of other higher-order nonlinear optical effects which have recently received a great deal of attention. For example, two-photon absorption has recently been used to study high-lying atomic states (Ducas *et al.*, 1975), and has become a common spectroscopic technique for study of optical properties of materials (see, for example, Worlock, 1972; Bredikhin *et al.*, 1973; Stafford and Sondergeld, 1974; Lee and Fan, 1974; Drucker and McClain, 1974). Selective multiphoton molecular dissociation is perhaps the most efficient method known for laser-induced isotope separation (Ambartzumian and Letokhor, 1974, 1975; Lyman *et al.*, 1975). Here, because of space limitation, we shall discuss only briefly the problems of multiphoton ionization and optical breakdown in gases and in solids by cascade ionization.

In the last three years a large number of theoretical and experimental papers on the subject of multiphoton ionization have appeared in the literature. The surge of interest comes because of the potential applications of multiphoton ionization to isotope separation (see, for example, Tuccio *et al.*, 1974), generation of spin-polarized electrons (Lambropoulos, 1973), analysis of optical breakdown, etc. The advent of tunable dye lasers has also made the study of multiphoton ionization more interesting and meaningful, since the more quantitative and subtle aspects of the problem can now be checked out experimentally.

Multiphoton ionization was first studied theoretically in connection with optical breakdown in gases (Bunkin and Prokhorov, 1964; Keldysh, 1964; Gold and Bebb, 1965). It was shown from higher-order perturbation calculations that multiphoton ionization can release enough free electrons to start cascade ionization and hence optical breakdown (Bebb and Gold, 1966). While the perturbation calculations are simple and straightforward, they are only valid when the laser intensity is sufficiently low and the intermediate states in the multiphoton transitions are sufficiently far away from resonances. In the more general cases, the effects of level shifts and line broadening induced by the strong laser field may have appreciable effect on the multiphoton ionization rate (Voronov *et al.*, 1966; Voronov, 1967). This is especially true for near-resonant multiphoton ionization processes with a laser intensity of about 10^{11} W/cm^2 or higher. More recent calculations (Gontier and Trahin, 1973; Chang and Stehle, 1973; Lambropoulos, 1974) have actually shown that the field-induced level shifts and line broadening contribute significantly to the multiphoton ionization probability. With intermediate states close to resonances, one may even find electric-quadrupole transitions to be important in some cases (P. Lambropoulos *et al.*, 1975), as has been recently demonstrated by M. Lambropoulos *et al.* (1975).

Quantitative experimental studies of multiphoton ionization essentially began in 1970 (Agostini *et al.*, 1970; Kishi and Okuda, 1971; Fox *et al.*, 1971; Bakos *et al.*, 1972; Delone *et al.*, 1972). Using a Q-switched Nd glass laser, Held *et al.* (1972) have studied multiphoton ionization of Cs atoms. While theoretically it would require

four photons to ionize a Cs atom, the experimental results seem to suggest a three-photon ionization process. It turns out that the Nd laser beam can first resonantly excite the $6f$ state of Cs by a three-photon process and then the excited Cs atom is ionized by a subsequent one-photon process. With a tunable Nd laser, Held *et al.* (1973) have also studied the dispersion of multiphoton ionization of Cs atoms by tuning the laser frequency over the three-photon $5s$-$6f$ resonant transition. They obtained an asymmetric curve for the ionization probability versus the laser frequency and also an anomaly in the dependence of ionization probability on laser intensity in a certain range of laser frequencies. Their results have now been successfully explained by Chang and Stehle (1973), taking into account the field-induced level shift and line broadening. More recently, multiphoton ionization of Cs has also been studied with the help of a tunable dye laser (Popescu *et al.*, 1974).

If the laser beam is sufficiently intense, than even n-photon ionization with n much larger than 1 can be observed. Thus, LuVan *et al.* (1972; 1973) have observed effective six-photon ionization of atomic hydrogen and 11-photon and 12-photon ionizations of molecular hydrogen in producing H^+ and H_2^+, respectively. Lecompte *et al.* (1975) have observed 11-photon ionization of Xe atoms. The experimental results of such higher-order multiphoton processes usually depend critically on the mode structure of the laser beam. A multimode laser beam should yield a much higher ionization probability than a single-mode laser beam (Ducuing and Bloembergen, 1964). Lecompte *et al.* (1975) have shown experimentally that, in the 11-photon ionization of Xe atoms, a laser beam with 100 longitudinal modes leads to an ionization probability $10^{6.9\pm0.3}$ times larger than a single-mode laser beam.

On the dependence of multiphoton ionization on laser polarization, Agostini and Bensoussan (1974) have conducted an experiment on resonant three-photon ionization of potassium with circularly and linearly polarized light. The frequency of the dye laser was tuned through two-photon resonances with the $6S_{1/2}$ and $4D_{3/2,5/2}$ states. Their results are in good agreement with the predicted polarization dependence from the theory of multiphoton ionization (Lambropoulos, 1972; Klarsfeld and Marquet, 1972). Lambropoulos (1973) has also predicted that multiphoton ionization of unpolarized atoms with circularly polarized light can effectively produce highly polarized electrons. Successful experimental demonstrations of the prediction have not yet been reported.

We have assumed in the above discussion of multiphoton ionization that the laser beam interacts with individual atoms independent of one another. This is the case if the gas pressure is sufficiently low ($\sim10^{-3}$ Torr) and the laser pulse width ($\sim10^{-8}$ sec) is appreciably shorter than the time interval between atomic collisions ($\sim10^{-6}$ sec). Also, the electron mean free path (~10 cm) is much longer than the size of the focal volume ($\sim10^{-2}$ cm) so that the secondary effect of ionization by electron collisions with atoms can be neglected. Under these conditions, multiphoton ionization is the only operating mechanism for ionization of a gas medium.

At higher gas pressures, free electrons released from atoms by multiphoton ionization can absorb photons by collisions with atoms (inverse bremsstrahlung). From inverse bremsstrahlung, an electron can attain enough energy capable of ionizing an atom to release another electron. This electron multiplication process may then lead to avalanche or cascade ionization by electrons. As soon as the ionization becomes appreciable, the incoming light can be readily absorbed by electrons via free-free transitions in the field of ions. This causes intense heating of the electron plasma, and consequently a rapid hydrodynamic expansion of the plasma in the form of a spherical shock wave. The phenomenon is known as optical breakdown. Experimentally, when this happens, a spark suddenly shows up in the medium (Maker *et al.*, 1963). Immediately, after the initial breakdown, the laser beam is preferentially absorbed by that part of the shock wave which is moving towards the laser. As a result, the spark appears to propagate against the laser beam (Ramsden and Davis, 1964).

Laser-induced gas breakdown has always been a subject of considerable research since its first observation. Raizer (1965) has pointed out in an early review article that either multiphoton ionization or cascade ionization is responsible for the initial stage of breakdown. At high gas pressures, cascade ionization is most likely the dominant mechanism. As a first approximation, one could perhaps describe optical cascade ionization by simply extending the classical theory of microwave cascade ionization (see, for example, Brown, 1956) to the optical frequencies (see Raizer, 1965; DeMichelis, 1969, and references therein). However, unlike the microwave case, the optical photon energy is clearly not negligible in comparison with the electron energy. As this is a quantum effect, it is not included in the classical theory. Recently, Kroll and Watson (1972) have taken the effect into account by using a modified Boltzmann transport equation to describe the dynamic electron distribution in the cascade process. They have carried out a detailed theoretical study of cascade breakdown of air by a laser beam. Their results appear to be in good agreement with experimental observations.

Experiments on laser-induced gas breakdown often deal with the breakdown threshold as a function of various parameters such as gas pressure, laser frequency, focal volume, etc. In the early years, the results were often complicated by the unknown multimode structure of the laser beam and the uncontrolled submicroscopic absorbing particles in the gas media (see the review articles of Raizer, 1965; DeMichelis, 1969; see also Bunkin and Savranskii, 1974). More recent experiments were designed to have more control of the experimental situation (see, for example, Smith, 1971; Berger and Smith, 1972; Brown and Smith, 1973; Yablonovitch, 1973 a, b; Ireland *et al.*, 1974). Although many quantitative aspects of optical breakdown, including factors which determine the breakdown threshold, are still not well understood, a good qualitative picture can now be drawn. In most cases, the breakdown threshold is determined by the submicroscopic absorbing particles in the medium which provide the first few electrons for the initiation of cascade ionization. The threshold becomes much higher if these submicroscopic particles are eliminated (Yablonovitch, 1973a; Boni and Meskan, 1975). In this latter case, the first electrons are presumably pro-

vided by multiphoton ionization, and the breakdown becomes intrinsic. The cascade ionization rate η seems to obey a similarity principle described by (see Yablonovitch, 1973b, and references therein)

$$\eta/p = f[E_{\rm rms}/p(1+\omega^2\tau^2)]\,, \tag{12.1}$$

where f is a characteristic function for each molecular species, p is the pressure, $E_{\rm rms}$ is the root-mean-square field, ω is the laser frequency, and τ is the momentum transfer collision time. A better comparison with the detailed theoretical calculations (such as those of Kroll and Watson, 1972) will require more quantitative experimental data.

After the initial breakdown, the discharge propagates and the plasma strongly absorbs the incoming light. Interaction of a laser beam with an expanding plasma and the resultant heating of the plasma pose a difficult problem, but it is clearly of great importance for the understanding of laser-induced fusion. We shall not dwell on this problem here, but simply refer the reader to the ever expanding literature (see, for example, the review articles by Raizer, 1965; DeMichelis, 1969; Krokhin, 1972; the conference proceedings edited by Schwarz and Horz, 1969; 1971; 1973; Yamanaka and Schwarz, 1973; Caldinola and Knoepfel, 1971; abstracts of the VIII International Quantum Electronics Conference, 1974; the most recent experimental papers by Wang and Davis, 1973; Yablonovitch, 1973a; 1974; Johnson and Chu, 1974, etc.).

Optical breakdown can also occur in transparent solids (we shall not consider opaque solids here.) This is a problem of great technical importance in laser optics. An understanding of the problem is essential to the design of optical materials and systems which can withstand higher laser power. In the early days of investigation of optical breakdown in solids (Maker *et al.*, 1963), the experimental results also suffered from complications due to the unknown multimode structure of the laser beam and absorbing inclusions in solids. In addition, self-focusing often dominated laser propagation in solids and determined the breakdown threshold.

The above difficulties can be dealt with by using a single-mode laser with a tight focusing to avoid self-focusing and by examining the breakdown results to distinguish intrinsic breakdown from extrinsic breakdown due to absorbing inclusion (Yablonovitch, 1971). The intrinsic breakdown threshold can thus be measured. The following experimental results have been obtained. The breakdown does not seem to occur at a definite laser intensity, but shows some statistical fluctuations (Bass and Barrett, 1972; 1973; Fradin *et al.*, 1973). However, the statistical spread is often so narrow that one can still talk about a breakdown threshold. The breakdown threshold for wide-gap insulators is nearly independent of the laser wavelength down to 1.06 μm and agrees well with the dc breakdown threshold within the experimental accuracy (Yablonovitch, 1971; Fradin *et al.*, 1973; Fradin and Bass, 1973b). It may show some slight increase at 0.69 μm, but conclusive experiments at shorter wavelengths have not yet been carried out. It also has a systematic variation among compounds of the same class of structure, for example, alkali halide compounds (Yablonovitch, 1971; Fradin *et al.*, 1973; Fradin and Bass, 1973b). The breakdown intensity threshold increases by two orders of magnitude as the laser pulse width reduces from ~10 nsec to ~10 psec (Fradin *et al.*, 1973; Smith *et al.*, 1975).

Here again, the possible mechanisms for breakdown are multiphoton ionization (Braünlich *et al.*, 1975; Baer *et al.*, 1974) and avalanche or cascade ionization. If, however, the photon energy is much less than the band gap energy, the probability of multiphoton ionization should be negligibly small. Avalanche ionization is then the only dominant mechanism (Yablonovitch and Bloembergen, 1972). The initial conduction electron density in solids, unlike that in gases, is at least 10^8 electrons/cm^3, resulting from photoionization or thermal ionization from donor levels. Therefore one does not need multiphoton ionization as an initiating mechanism to start avalanche ionization. Nevertheless, the number of initial electrons in the focal volume ($\sim 10^{-7}$ cm^3) may still be quite small. This can then lead to statistical fluctuations in the buildup of avalanche breakdown (Bass and Barrett, 1972; 1973). A simple rate equation for electron density appears to give a reasonable description of electron multiplication in the avalanche process (Bloembergen, 1974). According to this equation, the electron multiplication should decrease exponentially when the laser pulse width is reduced. Using simplifying assumptions, Yablonovitch and Bloembergen (1972) have derived a relation between the breakdown threshold $E_T(\omega)$ at ω and the dc breakdown threshold $E_T(0)$:

$$E_T(\omega) = E_T(0)[1+\omega^2\tau_{\rm eff}^2]^{1/2}\,, \tag{12.2}$$

where $\tau_{\rm eff}$ is an effective electron collision time which may be as short as 10^{-15} sec. This would then explain why the observed breakdown threshold appears to be independent of the laser frequency. A more rigorous theory, presumably derived from a modified Boltzmann transport equation for electrons, is not yet available.

The same breakdown process should also occur in laser-induced surface damage. One therefore expects the same breakdown threshold for the surface as for the bulk. Experimentally, it has been found that the surface breakdown threshold is usually much lower. In most cases, this is due to contamination of the surface by absorbing dust particles. For a chemically clean surface, the lower threshold can be due to scratches or pores on the surface since the field strength at these imperfection sites is much higher than that in the bulk (Bloembergen, 1973). It has indeed been demonstrated experimentally that by superpolishing the surface, one can raise the damage threshold significantly to approach the bulk damage threshold (Giuliano, 1972; Fradin and Bass, 1973a).

We have only been able to present here a brief outline of optical breakdown in solids. For more detail, we refer the reader to the review articles by Bloembergen (1974) and by Fradin (1973), and the conference proceedings on laser-induced damage in optical materials (NBS special publications, 1970–75).

XIII. CONCLUSIONS

We have presented in this paper a general review of all the major subfields of nonlinear optics. Our aim was to give a broad evaluation of the recent advances. While

discoveries of new nonlinear optical effects have not been numerous in recent years, the general understanding of the known effects has been dramatically improved. New material systems as effective nonlinear media have been investigated, and possible applications have been explored. In the future, the study of nonlinear optics is expected to become more quantitative and more sophisticated. The main interest of research will presumably be in areas of promise for useful applications.

ACKNOWLEDGMENT

Supported by the U. S. Energy Research and Development Administration.

REFERENCES

Abella, I. D., N. A. Kurnit, and S. R. Hartmann, 1966, Phys. Rev. **141**, 391.

Abella, I. D., 1969, in *Progress in Optics*, edited by E. Wolf (North-Holland, Amsterdam), Vol. 7.

Abragam, A., 1961, *Principles of Nuclear Magnetism* (Oxford University, Oxford).

Agostini, P., G. Barjot, G. Mainfray, C. Manus, and J. Thebault, 1970, IEEE J. Quantum Electron. **6**, 782.

Agostini, P., and P. Bensoussan, 1974, Appl. Phys. Lett. **24**, 216.

Akhmanov, S. A., and R. V. Khokhlov, 1964, *Problemy Nelineinoi Optiki* (Academy of Sciences of the U.S.S.R., Institute of Scientific Information) [*Problems of Nonlinear Optics*, translated by N. Jacobi and R. Sen, 1972 (Gordon and Breach, New York)].

Akhmanov, S. A., A.P. Sukhorukov, and R. V. Khokhlov, 1967, Usp. Fiz. Nauk **93**, 19 [Sov. Phys.—Usp. **93**, 609 (1968)].

Akhmanov, S. A., and A. P. Sukhorukov, 1967, Zh. Eksp. Teor. Fiz. Pis'ma Red. **5**, 109 [JETP Lett. **5**, 87 (1967)].

Akhmanov, S. A., V. G. Dmitriev, A. I. Kovrigin, N. I. Koroteev, V. G. Tunkin, and A. I. Kholodnykh, 1972, Zh. Eksp. Teor. Fiz. Pis'ma Red. **15**, 600 [JETP Lett. **15**, 425 (1972)].

Akhmanov, S. A., R. V. Khokhlov, and A. P. Sukhorukov, 1972, in *Laser Handbook*, edited by F. T. Arecchi and E. O. Schulz-Dubois (North-Holland, Amsterdam), p. 1151.

Akhmanov, S. A., N. I. Koroteev, and A. I. Kholodnykh, 1974, J. Raman Spectrosc. **2**, 239.

Alashkevich, V. A., S. A. Akhmanov, A. P. Sukhorukov, and A. M. Khachatryan, 1971, Zh. Eksp. Teor. Fiz. Pis'ma Red. **13**, 55 [JETP Lett. **13**, 36 (1971)].

Alcock, A. J., C. DeMichelis, V. V. Korobkin, and M. C. Richardson, 1969, Appl. Phys. Lett. **14**, 145.

Alcock, A. J., C. DeMichelis, and M. C. Richardson, 1970, IEEE J. Quantum Electron. **QE-6**, 622.

Alfano, R. R., and S. L. Shapiro, 1971a, Phys. Rev. Lett. **26**, 1247.

Alfano, R. R., and S. L. Shapiro, 1971b, Chem. Phys. Lett. **8**, 43.

Alfano, R. R., and S. L. Shapiro, 1972, Phys. Rev. Lett. **29**, 1655.

Allen, L., and J. H. Eberly, 1975, *Optical Resonance and Two-Level Atoms* (Wiley, New York). Up-to-date detailed descriptions of all coherent optical effects in systems of two-level atoms can be found in this book and the references therein.

Ambartzumian, R. V., and V. S. Letokhov, 1974, JETP Lett. **20**, 897.

Ambartzumian, R. V., and V. S. Letokhov, 1975, Laser Focus **11**, 48.

Ambartzumian, R. V., V. S. Letokhov, E. A. Ryabor, and N. V. Chekalin, 1974, JETP Lett. **20**, 273.

Anderson, D. B., and J. T. Boyd, 1971, Appl. Phys. Lett. **19**, 266.

Andrews, R. A., 1971, IEEE J. Quantum Electron. **QE-7**, 523.

Arecchi, F. T., and E. Courtens, 1970, Phys. Rev. A **2**, 1730.

Armstrong, J., N. Bloembergen, J. Ducuing, and P. S. Pershan, 1962, Phys. Rev. **127**, 1918.

Armstrong, J. A., and J. J. Wynne, 1974, Phys. Rev. Lett. **33**, 1183.

Arnush, D., B. Fried, C. Kennel, K. Nishikawa, and A. Y. Wong, 1972, University of California, Los Angeles, Report No. PPG-139 (unpublished).

Askar'yan, G. A., 1962, Zh. Eksp. Teor. Fiz. **42**, 1567; **42**, 1672 [Sov. Phys. JETP **15**, 1088; **15**, 1161 (1962)].

Baer, V. M., A. N. Savehenko, and E. A. Sviridenkor, 1974, Zh. Eksp. Teor. Fiz. **66**, 913 [Sov. Phys. JETP **39**, 443].

Bakhramov, S. A., U. G. Gulyamov, K. N. Drabovich, and Ya. Z. Faizullaev, 1975, JETP Lett. **21**, 102.

Baldis, H. A., H. Pepin, T. W. Johnson, and K. J. Parbhakar, 1975, Phys. Rev. Lett. **35**, 37.

Baldis, H. A., H. Pepin, T. W. Johnson, and K. Papadopoulos, 1975, Phys. Rev. Lett. **35**, 37.

Baldwin, G. C., 1969, *An Introduction to Nonlinear Optics* (Plenum, New York).

Bakos, J., A. Kiss, L. Szabo, and M. Tendler, 1972, Phys. Lett. A **39**, 283; 317; **41**, 163.

Barak, S., M. Rokni, and S. Yatsiv, 1969, IEEE J. Quantum Electron. **QE-5**, 448.

Barnard, T. W., 1973, Phys. Rev. A **7**, 373.

Bass, M., and H. H. Barrett, 1972, IEEE J. Quantum Electron. **QE-8**, 338.

Bass, M., and H. H. Barrett, 1973, Appl. Opt. **12**, 690.

Bebb, H. B., and A. Gold, 1966, Phys. Rev. **143**, 1.

Begley, R. F., A. B. Harvey, and R. L. Byer, 1974, Appl. Phys. Lett. **25**, 387.

Bell, M. I., 1972, in *Electronic Density of States*, edited by L. H. Bennett, National Bureau of Standards (U.S.) Spec. Publ. No. 323 (U.S. GPO, Washington, D.C., 1971), p. 757.

Bell, M. I., 1972, Phys. Rev. B **6**, 516.

Bellard, P., C. DeMichelis, and M. Mattioli, 1971, Opt. Commun. **4**, 50.

Berger, P.J. and D. C. Smith, 1972, Appl. Phys. Lett. **21**, 167.

Berman, P. R., J. M. Levy, and R. G. Brewer, 1975, Phys. Rev. A **11**, 1668.

Biraben, F., B. Cagnac, and G. Grynberg, 1974, Phys. Rev. Lett. **32**, 643.

Bischel, W. K., P. J. Kelley, and C. K. Rhodes, 1975, Phys. Rev. Lett. **34**, 300.

Biskamp, D., and H. Welter, 1975, Phys. Rev. Lett. **34**, 312.

Bjorkholm, J. E., and P. F. Liao, 1974, Phys. Rev. Lett. **33**, 128.

Bjorkholm, J. E., 1966, Phys. Rev. **142**, 126.

Bjorkholm, J. E., and A. Ashkin, 1974, Phys. Rev. Lett. **32**, 129.

Bloembergen, N., 1965, *Nonlinear Optics* (Benjamin, New York).

Bloembergen, N., R. K. Chang, and J. Ducuing, 1966, in *Physics of Quantum Electronics*, edited by P. L. Kelley, B. Lax, and P. E. Tannenwald (McGraw-Hill, New York), p. 67.

Bloembergen, N., and Y. R. Shen, 1966, Phys. Rev. **141**, 298.

Bloembergen, N., 1967, Am. J. Phys. **35**, 989.

Bloembergen, N., R. K. Chang, S. S. Jha, and C. H. Lee, 1968, Phys. Rev. **174**, 183.

Bloembergen, N., and A. J. Sievers, 1970, Appl. Phys. Lett. **17**, 483.

Bloembergen, N., 1973, Appl. Opt. **12**, 661.

Bloembergen, N., 1974, IEEE J. Quantum Electron. **QE-10**, 375.

Bloom, D. M., J. T. Yardley, J. F. Young, and S. E. Harris, 1974, Appl. Phys. Lett. **24**, 427.

Bloom, D. M., G. W. Bekkers, J. F. Young, and S. E. Harris, 1975, Appl. Phys. Lett. **26**, 687.

Bobin, J. L., M. Decroisette, B. Meyer, and Y. Vitel, 1973,

Phys. Rev. Lett. **30**, 594.
Boni, A. A., and D. A. Meskan, 1975, Opt. Commun. **14**, 115.
Boyd, G. D., A. Ashkin, J. M. Dziedzic, and D. A. Kleinman, 1965, Phys. Rev. **137**, 1305.
Boyd, G. D., and D. A. Kleinman, 1968, J. Appl. Phys. **39**, 3597.
Boyd, G. D., T. J. Bridges, C. K. N. Patel, and E. Buchler, 1972, Appl. Phys. Lett. **21**, 553.
Braünlich, P., A. Schmid, and P. Kelly, 1975, Appl. Phys. Lett. **26**, 150.
Bredikhin, V. I., M. D. Galanin, and V. N. Genkin, 1973, Usp. Fiz. Nauk **110**, 3 [Sov. Phys.—Usp. **16**, 299 (1973)].
Brewer, R. G., and J. R. Lifsitz, 1966, Phys. Lett. **23**, 79.
Brewer, R. G., and C. H. Townes, 1967, Phys. Rev. Lett. **18**, 196.
Brewer, R. G., J. R. Lifsitz, E. Garmire, R. Y. Chiao, and C. H. Townes, 1968, Phys. Rev. **166**, 326.
Brewer, R. G., and R. L. Shoemaker, 1971, Phys. Rev. Lett. **27**, 631.
Brewer, R. G., and R. L. Shoemaker, 1972, Phys. Rev. A **6**, 2001.
Brewer, R. G., and E. L. Hahn, 1973, Phys. Rev. A **8**, 464.
Brewer, R. G., and E. L. Hahn, 1975, Phys. Rev. A **11**, 1641.
Brewer, R. G., R. L. Shoemaker, and S. Stenholm, 1974, Phys. Rev. Lett. **33**, 63.
Bridges, T. J., and T. Y. Chang, 1969, Phys. Rev. Lett. **22**, 811.
Bridges, T. J., and A. R. Strnad, 1972, Appl. Phys. Lett. **20**, 382.
Bridges, T. J., and V. T. Nguyen, 1973, Appl. Phys. Lett. **23**, 107.
Brignall, N., R. A. Wood, C. R. Pidgeon, and B. S. Wherrett, 1974, Opt. Commun. **12**, 17.
Brown, F., R. E. Parks, and A. M. Sleeper, 1965, Phys. Rev. Lett. **14**, 1029.
Brown, R. T., and D. C. Smith, 1973, Appl. Phys. Lett. **22**, 245.
Brown, S. C., 1956, in *Encyclopedia of Physics*, edited by S. Flügge (Springer-Verlag, Berlin), Vol. XXII.
Brown, T. L., and R. A. Wolff, 1972, Phys. Rev. Lett. **29**, 362.
Brueck, S. R. J., and A. Mooradian, 1971, Appl. Phys. Lett. **18**, 229.
Bunkin, F. V., and A. M. Prokhorov, 1964, Zh. Eksp. Teor. Fiz. **46**, 1090 [Sov. Phys.—JETP **19**, 739 (1964)].
Bunkin, F. V., I. K. Krasyuk, V. M. Marchenko, P. P. Pashinin, and A. M. Prokhorov, 1971, Zh. Eksp. Teor. Fiz. **60**, 1326 [Sov. Phys.—JETP **33**, 717].
Bunkin, F. V., and V. V. Savranskii, 1974, Zh. Eksp. Teor. Fiz. **38**, 2185 [Sov. Phys.—JETP **38**, 1091 (1974)].
Burns, W. K., and R. A. Andrews, 1972, IEEE J. Quantum Electron. **QE-8**, 549.
Burns, W. K., and R. A. Andrews, 1973, Appl. Phys. Lett. **22**, 143.
Burns, W. K., and A. B. Lee, 1974, Appl. Phys. Lett. **24**, 222.
Butcher, P. N., 1965, *Nonlinear Optical Phenomena* (Ohio State University , Columbus).
Byer, R. L., M. M. Choy, R. L. Herbst, D. S. Chemla, and R. S. Feigelson, 1974, Appl. Phys. Lett. **24**, 65.
Cagnac, B., G. Grynberg, and F. Biraben, 1973, J. Phys. (Paris) **34**, 845.
Carlsten, J. L., and P. C. Dunn, 1975, Opt. Commun. **14**, 8.
Carman, R. L., F. Shimizu, C. S. Wang, and N. Bloembergen, 1970, Phys. Rev. A **2**, 60.
Carman, R. L., and J. A. Fleck, 1972, Appl. Phys. Lett. **20**, 290.
Carman, R. L., and M. E. Mack, 1972, Phys. Rev. A **5**, 341.
Carmel, Y., J. Ivers, R. E. Kribel, and J. Nation, 1974, Phys. Rev. Lett. **33**, 1278.
Chang, C. S., and P. Stehle, 1973, Phys. Rev. Lett. **30**, 1283.
Chang, R. K., J. Ducuing, and N. Bloembergen, 1965, Phys. Rev. Lett. **15**, 415.
Chang, T. Y., V. T. Nguyen, and C. K. N. Patel, 1968, Appl. Phys. Lett. **13**, 357.
Chen, B. U., C. L. Tang, and J. M. Telle, 1974, Appl. Phys. Lett. **25**, 495.
Cheo, P. K., and C. H. Wang, 1970, Phys. Rev. A **1**, 225.
Chiao, R. Y., E. Garmire, and C. H. Townes, 1964, Phys. Rev. Lett. **13**, 479; Erratum, 1965, Phys. Rev. Lett. **14**, 1056.
Chiao, R. Y., M. A. Johnson, S. Krinsky, H. A. Smith, C. H. Townes, and E. Garmire, 1966, IEEE J. Quantum Electron. **QE-2**, 467.
Cho, A. Y., 1971, Appl. Phys. Lett. **19**, 467.
Coffinet, J. P., and F. DeMartini, 1969, Phys. Rev. Lett. **27**, 23.
Cohen, B. I., A. N. Kaufman, and K. M. Watson, 1972, Phys. Rev. Lett. **29**, 581.
Compaan, A., and I. D. Abella, 1971, Phys. Rev. Lett. **27**, 23.
Condon, E. U., and G. H. Shortley, 1951, *The Theory of Atomic Spectra* (Cambridge University, London).
Conwell, E. M., 1973, IEEE J. Quantum Electron. **QE-9**, 867.
Coulson, C. A., 1961, *Valence* (Oxford University, London).
Courtens, E., 1972, in *Laser Handbook*, edited by F. T. Arecchi and E. O. Schulz-Dubois (North-Holland, Amsterdam), p. 1259.
Dabby, F. W., and J. R. Whinnery, 1968, Appl. Phys. Lett. **13**, 28.
Dawes, E. L., and J. H. Marburger, 1969, Phys. Rev. **179**, 862.
deGennes, P. G., 1974, *Physics of Liquid Crystals* (Clarendon, Oxford).
Dekker, C. D., and F. K. Tittel, 1973, Appl. Phys. Lett. **22**, 41.
Delone, G., N. B. Delone, and G. K. Piskova, 1972, Zh. Eksp. Teor. Fiz. **62**, 1272 [Sov. Phys.—JETP **35**, 672 (1972)].
DeMartini, F., G. P. Giuliani, and E. Santamato, 1972, Opt. Commun. **5**, 126.
DeMichelis, C., 1969, IEEE J. Quantum Electron. **QE-5**, 188.
Denbigh, K. G., 1940, Trans. Faraday Soc. **36**, 936.
DeSilets, C. S., and C. K. N. Patel, 1973, Appl. Phys. Lett. **22**, 543.
Dicke, R. H., 1954, Phys. Rev. **93**, 99.
Diels, J. C., and E. L. Hahn, 1973, Phys. Rev. A **8**, 1084.
Drucker, R. P., and W. M. McClain, 1974, J. Chem. Phys. **61**, 2609; 2616.
Dubois, D. F., and M. V. Goldman, 1965, Phys. Rev. Lett. **14**, 544.
Ducas, T. W., M. G. Littman, R. R. Freeman, and D. Kleppner, 1975, Phys. Rev. Lett. **35**, 366.
Ducuing, J., and N. Bloembergen, 1964, Phys. Rev. **133**, 1493.
Ducuing, J., and C. Flytzanis, 1971, in *Optical Properties of Solids*, edited by F. Abelès (North-Holland, Amsterdam).
Dyshko, A. L., V. N. Lugovoi, and A. M. Prokhorov, 1967, Zh. Eksp. Teor. Fiz. Pis'ma Red. **6**, 655 [JETP Lett. **6**, 146 (1967)].
Eidmann, K., and R. Sigel, 1975, Phys. Rev. Lett. **34**, 799.
Eng, R. S., A. Mooradian, and H. R. Fettermann, 1974, Appl. Phys. Lett. **25**, 453.
Esaki, L., 1974, Jpn. J. Appl. Phys. Suppl. **43**, 452.
Esaki, L., and L. L. Chang, 1974, Phys. Rev. Lett. **33**, 495.
Faris, D. W., K. A. Gehring, P. L. Richards, and Y. R. Shen, 1969, Phys. ReV. **180**, 363.
Faris, D. W., P. L. Richards, Y. R. Shen, and K. H. Yang, 1971, Phys. Rev. A **3**, 2148.
Feld, M. S., and A. Javan, 1969, Phys. Rev. **177**, 540.
Feynman, R. P., F. L. Vernon, and R. W. Hellwarth, 1957, J. Appl. Phys. **28**, 49.
Fleck, J. A., and P. L. Kelley, 1969, Appl. Phys. Lett. **15**, 313.
Fleck, J. A., and C. Layne, 1973, Appl. Phys. Lett. **22**, 467.
Flytzanis, C., and J. Ducuing, 1969, Phys. Rev. **178**, 1218.
Fong, C. Y., and Y. R. Shen, 1975, Phys. Rev. (to be published).

Forslund, D. W., J. M. Kindel, and E. L. Lindman, 1973, Phys. Rev. Lett. **30**, 739.
Foster, K. L., S. Stenholm, and R. G. Brewer, 1974, Phys. Rev. A **10**, 2318.
Fox, A. G., and P. W. Smith, 1967, Phys. Rev. Lett. **18**, 826.
Fox, A. G., S. E. Schwarz, and P. W. Smith, 1968, Appl. Phys. Lett. **12**, 371.
Fox, R. A., R. M. Kogan, and E. J. Robinson, 1971, Phys. Rev. Lett. **26**, 1416.
Fradin, D. W., 1973, Technical Report 643, Harvard University.
Fradin, D. W., and M. Bass, 1973a, Appl. Phys. Lett. **22**, 157.
Fradin, D. W. and M. Bass, 1973b, Appl. Phys. Lett. **22**, 206.
Fradin, D. W., N. Bloembergen, and J. P. Letellier, 1973, Appl. Phys. Lett. **22**, 635.
Fradin, D. W., E. Yablonovitch, and M. Bass, 1973, Appl. Opt. **12**, 700.
Franken, P. A., A. E. Hall, C. W. Peters, and G. Weinreich, 1961, Phys. Rev. Lett. **7**, 118.
Frey, R., and F. Pradere, 1974, Opt. Commun. **12**, 98.
Frova, A., M. A. Duguay, C. G. B. Garrett, and S. L. McCall, 1969, J. Appl. Phys. **40**, 3969.
Fuchs, V., C. R. Neufeld, J. Teichmann, and A. G. Englehardt, 1973, Phys. Rev. Lett. **31**, 1110.
Galeev, A. A., G. Laval, T. M. O'Neil, M. N. Rosenbluth, and R. Z. Sagdeev, 1973, Zh. Eksp. Teor. Fiz. Pis'ma Red. **17**, 35 [JETP Lett. **17**, 48 (1973)].
Gelbwachs, J., R. H. Pantell, H. E. Puthoff, and J. M. Yarborough, 1969, Appl. Phys. Lett. **14**, 258.
Gibbs, H. M., and R. E. Slusher, 1970, Phys. Rev. Lett. **24**, 638.
Gibbs, H. M., and R. E. Slusher, 1972, Phys. Rev. A **6**, 2326.
Gibbs, H. M., 1973, Phys. Rev. A **8**, 446.
Gibbs, H. M., G. G. Churchill, and G. J. Salamo, 1974, Opt. Commun. **12**, 396.
Giuliano, C. R., and J. H. Marburger, 1971, Phys. Rev. Lett. **27**, 905.
Giuliano, C. R., 1972, Appl. Phys. Lett. **21**, 39.
Gold, A., and H. B. Bebb, 1965, Phys. Rev. Lett. **14**, 60.
Goldberg, V. N., V. I. Talanov, and R. E. Irm, 1967, Izv. Vyssh. Uchebn. Zaved. Radiofiz. **10**, 674.
Goldman, L. M., J. Soures, and M. J. Lubin, 1973, Phys. Rev. Lett. **31**, 1184.
Gontier, Y., and M. Trahin, 1973, Phys. Rev. A **7**, 1899.
Gordon, J. P., C. H. Wang, C. K. N. Patel, R. E. Slusher, and W. J. Tomlison, 1969, Phys. Rev. **179**, 294.
Gornik, W., D. Kaiser, W. Lange, J. Luther, and H. H. Schulz, 1972, Opt. Commun. **6**, 327.
Granatstein, V. L., M. Herndon, R. K. Parker, and S. P. Schlesinger, 1974, IEEE J. Quantum Electron. **10**, 651.
Grieneisen, H. P., J. Goldhar, N. A. Kurnit, and A. Javan, 1972, Appl. Phys. Lett. **21**, 559.
Grischkowsky, D., 1970, Phys. Rev. Lett. **24**, 866.
Grischkowsky, D., and J. A. Armstrong, 1972, Phys. Rev. A **6**, 1566.
Grischkowsky, D., 1973, Phys. Rev. A **7**, 2096.
Grischkowsky, D., E. Courtens, and J. Armstrong, 1973, Phys. Rev. Lett. **31**, 422.
Grischkowsky, D., 1974, Appl. Phys. Lett. **25**, 566.
Grischkowsky, D., E. Courtens, and J. A. Armstrong, 1974, in *Proceedings of Laser Spectroscopy*, edited by R. G. Brewer and A. Mooradian (Plenum, New York), p. 333.
Grischkowsky, D., and M. M. T. Loy, 1975, Appl. Phys. Lett. **26**, 156.
Hahn, E. L., 1950, Phys. Rev. **80**, 580.
Hall, J. L., and C. Bordé, 1973, Phys. Rev. Lett. **30**, 1101.
Hall, J. L., 1973, in *Atomic Physics 3*, edited by S. J. Smith and D. K. Walters (Plenum, New York), p. 615.
Hanna, D. C., B. Luther-Davies, H. N. Rutt, and R. C. Smith, 1972, Appl. Phys. Lett. **20**, 34.
Hanna, D. C., B. Luther-Davis, R. C. Smith, and R. Wyatt, 1974, Appl. Phys. Lett. **25**, 142.
Hänsch, T. W., I. S. Shahin, and A. L. Schawlow, 1972, Nat. Phys. Sci. **235**, 63.
Hänsch, T. W., 1973, in *Dye Lasers*, edited by F. P. Schäfer (Springer, Berlin), p. 174.
Hänsch, T. W., K. C. Harvey, G. Meisel, and A. L. Schawlow, 1974, Opt. Commun. **11**, 50.
Hänsch, T. W., M. H. Nayfeh, S. A. Lee, S. M. Curry, and I. S. Shahin, 1974, Phys. Rev. Lett. **32**, 1336.
Hänsch, T. W., S. A. Lee, R. Wallenstein, and C. Wieman, 1975, Phys. Rev. Lett. **34**, 307.
Hanson, E., 1975, private communication.
Haroche, S., J. A. Paisner, and A. L. Schawlow, 1973, Phys. Rev. Lett. **30**, 948.
Harris, S. E., 1973, Phys. Rev. Lett. **31**, 341.
Harris, S. E., J. F. Young, A. H. Kung, D. M. Bloom, and G. C. Bjorklund, 1974, in *Proceedings of the Laser Spectroscopy Conference*, edited by R. G. Brewer and A. Mooradian (Plenum, New York).
Harris, S. E., and D. M. Bloom, 1974, Appl. Phys. Lett. **24**, 229.
Harris, S. E., J. F. Young, D. M. Bloom, A. H. Kung, J. T. Yardley, and G. C. Bjorklund, 1974, in VIII International Quantum Electronics Conference (San Francisco), paper M5.
Harvey, K. C., R. T. Hawkins, G. Meisel, and A. L. Schawlow, 1975, Phys. Rev. Lett. **34**, 1073.
Hauchecorne, G., and G. Mayer, 1965, C. R. Acad. Sci. Ser. B **261**, 4014.
Heitler, W., 1954, *The Quantum Theory of Radiation* (Cambridge University, New York, 3d ed.), p. 192.
Held, B., B. Mainfray, C. Manus, and J. Morellec, 1972, Phys. Rev. Lett. **28**, 130.
Held, B., B. Mainfray, C. Manus, J. Morellec, and F. Sanchez, 1973, Phys. Rev. Lett. **30**, 423.
Henry, C. H., and C. G. B. Garrett, 1968, Phys. Rev. **171**, 1058.
Herbst, R. L., and R. L. Byer, 1971, Appl. Phys. Lett. **19**, 527.
Herbst, R. L., and R. L. Byer, 1972, VII International Quantum Electronics Conference (Montreal, Canada), paper L.9.
Herbst, R. L., and R. L. Byer, 1975, private communication.
Hercher, M., 1964, J. Opt. Soc. Am. **54**, 563.
Heritage, J. P., T. K. Gustafson, and C. H. Lin, 1975, Phys. Rev. Lett. **34**, 1299.
Hocker, G. B., and C. L. Tang, 1969, Phys. Rev. Lett. **21**, 591.
Hodgson, R. T., P. P. Sorokin, and J. J. Wynne, 1974, Phys. Rev. Lett. **32**, 343.
Hopf, F. A., G. L. Lamb, C. K. Rhodes, and M. O. Scully, 1971, Phys. Rev. A **3**, 758.
Huang, K., 1951, Nature **167**, 779.
Huang, K., 1951, Proc. R. Soc. Lond. A **208**, 352.
Ippen, E. P., 1970, Appl. Phys. Lett. **16**, 303.
Ippen, E. P., C. V. Shank, and T. K. Gustafson, 1974, Appl. Phys. Lett. **24**, 190.
Ireland, C. L. M., A. Yi, J. M. Aaron, and C. G. Morgan, 1974, Appl. Phys. Lett. **24**, 175.
Ito, H., N. Vesugi, and H. Inaba, 1974, Appl. Phys. Lett. **25**, 385.
Itzkan, I., and D. A. Leonard, 1975, Appl. Phys. Lett. **26**, 106.
Javan, A., and P. L. Kelley, 1966, IEEE J. Quantum Electron. **QE-2**, 470.
Jha, S. S., 1965, Phys. Rev. **140**, A2020.
Jha, S. S., and N. Bloembergen, 1968, Phys. Rev. **171**, 891.
Johnson, L. C., and T. K. Chu, 1974, Phys. Rev. Lett. **32**, 517.
Jones, W. J., and B. P. Stoicheff, 1964, Phys. Rev. Lett. **13**, 657.
Kachen, G. I., 1975, UCRL Report 51753 (Lawrence Livermore Laboratory, University of California).
Kaiser, W., and M. Maier, 1972, in *Laser Handbook*, edited by F. T. Arecchi and E. O. Schulz-Dubois (North-Holland, Amsterdam), p. 1077.

Kaufman, A. N., and B. I. Cohen, 1973, Phys. Rev. Lett. **30**, 1306.
Keldysh, L. V., 1964, Zh. Eksp. Teor. Fiz. **47**, 7 [Sov. Phys.—JETP **20**, 4 (1965)].
Kelley, P. L., 1965, Phys. Rev. Lett. **15**, 1005; erratum: 1966, Phys. Rev. Lett. **16**, 384.
Kelley, P. L., H. Kildal, and H. R. Schlossberg, 1974, VIII Quantum Electronics Conference (San Francisco), paper F.9.
Kerr, E. L., 1972, Phys. Rev. A **6**, 1162.
Kidder, R. E., 1971, in *Physics of High Energy Density*, Proceedings of the International School of Physics, "Enrico Fermi" Course XLIII, edited by P. Caldirola and H. Knoepfel (Academic, New York), p. 306.
Kishi, K., and T. Okuda, 1971, J. Phys. Soc. Jpn. **31**, 1289.
Klarsfeld, S., and A. Marquet, 1972, Phys. Rev. Lett. **29**, 79.
Klein, H. H., W. M. Manheimer, and E. Ott, 1973, Phys. Rev. Lett. **31**, 1187.
Kleinman, D. A., A. Ashkin, and G. Boyd, 1966, Phys. Rev. **145**, 338.
Kleinman, D. A., 1972, in *Laser Handbook*, edited by F. T. Arecchi and E. O. Schulz-Dubois (North-Holland, Amsterdam), p. 1229.
Krokhin, O. N., 1972, in *Laser Handbook*, edited by F. T. Arecchi and E. O. Schulz-Dubois (North-Holland, Amsterdam), p. 1371.
Korobkin, V. V., and A. J. Alcock, 1968, Phys. Rev. Lett. **21**, 1433.
Korobkin, V. V., A. M. Prokhorov, R. V. Serov, and M. Ya. Shchelev, 1970, Zh. Eksp. Teor. Fiz. Pis'ma Red. **11**, 153 [JETP Lett. **11**, 94 (1970)].
Kramer, S. D., F. G. Parsons, and N. Bloembergen, 1974, Phys. Rev. B **9**, 1853.
Kroll, N., A. Ron, and N. Rostoker, 1964, Phys. Rev. Lett. **13**, 83.
Kung, A. H., J. F. Young, G. C. Bjorklund, and S. E. Harris, 1972, Phys. Rev. Lett. **29**, 985.
Kung, A. H., J. F. Young, and S. E. Harris, 1973, Appl. Phys. Lett. **22**, 301.
Kurnit, N. A., I. D. Abella, and S. R. Hartman, 1964, Phys. Rev. Lett. **13**, 567.
Kurtz, S. K., and J. A. Giordmaine, 1969, Phys. Rev. Lett. **22**, 192.
Kurtz, S. K., 1972, in *Laser Handbook*, edited by F. T. Arecchi and E. O. Schulz-Dubois (North-Holland, Amsterdam), p. 923.
Lallemand, P., and N. Bloembergen, 1965, Phys. Rev. Lett. **15**, 1010.
Lamb, G. L., 1967, Phys. Lett. **25A**, 181.
Lamb, G. L., 1971, Rev. Mod. Phys. **43**, 99.
Lamb, W. E., 1964, Phys. Rev. **134**, A1429.
Lambropoulos, P., 1972, Phys. Rev. Lett. **28**, 585; **29**, 453.
Lambropoulos, P., 1973, Phys. Rev. Lett. **30**, 413.
Lambropoulos, P., 1974, Phys. Rev. A **9**, 1992.
Lambropoulos, P., G. Doolen, and S. P. Rountree, 1975, Phys. Rev. Lett. **34**, 636.
Lambropoulos, M., S. E. Moody, S. J Smith, and W. C. Linebeyer, 1975, Phys. Rev. Lett. **35**, 159.
Landau, L. D., and E. M. Lifshitz, 1960, *Electrodynamics of Continuous Media* (Pergamon, Oxford), p. 251.
Laubereau, A., D. von der Linde, and W. Kaiser, 1971, Phys. Rev. Lett. **27**, 802.
Laubereau, A., D. von der Linde, and W. Kaiser, 1972, Phys. Rev. Lett. **28**, 1162.
Laubereau, A., D. von der Linde, and W. Kaiser, 1973, Opt. Commun. **7**, 173.
Laubereau, A., L. Kirchner, and W. Kaiser, 1973, Opt. Commun. **9**, 182.
Laubereau, A., G. Kehl, and W. Kaiser, 1974, Opt. Commun. **11**, 74.
Laubereau, A., L. Greiter, and W. Kaiser, 1974, Appl. Phys. Lett. **25**, 87.
Lax, B., R. L. Aggarwal, and G. Favrot, 1973, Appl. Phys. Lett. **23**, 679.
Lax, B., and R. L. Aggarwal, 1974, J. Opt. Soc. Am. **64**, 533.
LeCompte, C., G. Mainfray, C. Manus, and F. Sanchez, 1975, Phys. Rev. A **11**, 1009.
Lee, C. C., and H. Y. Fan, 1974, Phys. Rev. B **9**, 3502.
Lee, N., R. L. Aggarwal, and B. Lax, 1974, Opt. Commun. **11**, 339.
Lee, P., D. V. Giovanelli, R. P. Godwin, and G. H. McCall, 1974, Appl. Phys. Lett. **24**, 406.
Lee, Y. C., and C. H. Su, 1966, Phys. Rev. **152**, 129.
Levenson, M. D., C. Flytzanis, and N. Bloembergen, 1972, Phys. Rev. B **6**, 3962.
Levenson, M. D., 1974, IEEE J. Quantum Electron. **QE-10**, 110.
Levenson, M. D., and N. Bloembergen, 1974, J. Chem. Phys. **60**, 1323.
Levenson, M. D., and N. Bloembergen, 1974, Phys. Rev. B **10**, 4447.
Levenson, M. D., and N. Bloembergen, 1974, Phys. Rev. Lett. **32**, 645.
Levine, B. F., 1969, Phys. Rev. Lett. **22**, 787.
Levine, B. F., 1973, Phys. Rev. B **7**, 2600 (and the references therein).
Levine, B. F., C. G. Bethea, and R. A. Logan, 1975, Appl. Phys. Lett. **26**, 375.
Liao, P. F., and J. E. Bjorkholm, 1975, Phys. Rev. Lett. **34**, 1.
Louie, S., and M. L. Cohen, 1975, private communications.
Lowdermilk, W. H., and G. I. Kachen, 1975, Appl. Phys. Lett. **27**, 133.
Loy, M. M. T., and Y. R. Shen, 1969, Phys. Rev. Lett. **22**, 994.
Loy, M. M. T., and Y R. Shen, 1970, Phys. Rev. Lett. **25**, 1333.
Loy, M. M. T., and Y. R. Shen, 1971, Appl. Phys. Lett. **19**, 285.
Loy, M. M. T., and Y. R. Shen, 1973, IEEE J. Quantum Electron. **QE-9**, 409.
Loy, M. M. T., 1974, Phys. Rev. Lett. **32**, 814.
Loy, M. M. T., 1975, Appl. Phys. Lett. **26**, 99.
Lugovoi, V. N., and A. M. Prokhorov, 1968, Zh. Eksp. Teor. Fiz. Pis'ma Red. **7**, 153 [JETP Lett. **7**, 117 (1968)].
Lukasik, J., and J. Ducuing, 1972, Phys. Rev. Lett. **28**, 1155.
LuVan, M., G. Mainfray, C. Manus, and I. Tugov, 1972, Phys. Rev. Lett. **29**, 1134.
LuVan, M., G. Mainfray, C. Manus, and I. Tugov, 1973, Phys. Rev. A **7**, 91.
Lyman, J. L., R. J. Jensen, J. Rink, C. P. Robinson, and S. D. Rockwood, 1975, Appl. Phys. Lett. **27**, 87.
Maier, M., W. Kaiser, and J. A. Giordmaine, 1966, Phys. Rev. Lett. **17**, 1275.
Maier, M., W. Kaiser, and J. A. Giordmaine, 1969, Phys. Rev. **177**, 580.
Maier, M., G. Wendl, and W. Kaiser, 1970, Phys. Rev. Lett. **24**, 352.
Maker, P. D., R. W. Terhune, and C. M. Savage, 1963, Proc. III International Quantum Electronics Conference, edited by P. Grivet and N. Bloembergen (Columbia University, New York), p. 1559.
Maker, P. D., and R. W. Terhune, 1965, Phys. Rev. **137**, A801.
Marburger, J. H., and E. L. Dawes, 1968, Phys. Rev. Lett. **21**, 556.
Max, C. E., J. Arons, and A. B. Langdon, 1974, Phys. Rev. Lett. **33**, 209.
McAllister, G., J. Marburger, and L. De Shazer, 1968, Phys. Rev. Lett. **21**, 1648.
McCall, S. L., and E. L. Hahn, 1967, Phys. Rev. Lett. **18**, 908.
McCall, S. L., and E. L. Hahn, 1969, Phys. Rev. **183**, 457.
McCall, S. L., and E. L. Hahn, 1970, Phys. Rev. A **2**, 861.
McFarlane, R. A., W. R. Bennet, and W. E. Lamb, 1963, Appl. Phys. Lett. **2**, 189.
McLaren, R. A., and B. P. Stoicheff, 1970, Appl. Phys. Lett. **16**, 140.

McQuillan, A. K., and B. P. Stoicheff, 1966, in *Physics of Quantum Electronics*, edited by P. L. Kelley, B. Lax, and P. E. Tannenwald (McGraw-Hill, New York), p. 192.
Miles, R. B., and S. E. Harris, 1971, Appl. Phys. Lett. **19**, 385.
Miles, R. B., and S. E. Harris, 1973, IEEE J. Quantum Electron. **QE-9**, 470.
Mooradian, A., S. R. J. Brueck, and F. A. Blum, 1970, Appl. Phys. Lett. **17**, 481.
Moya, F., S. A. J. Druet, and J. P. E. Taran, 1975, Opt. Commun. **13**, 169.
Neberzahl, I., and A. Szöke, 1974, Appl. Phys. Lett. **25**, 327.
Nguyen, V. T., and C. K. N. Patel, 1969, Phys. Rev. Lett. **22**, 463.
Nguyen, V. T., and T. J. Bridges, 1972, Phys. Rev. Lett. **29**, 359.
Nguyen, V. T., and T. J. Bridges, 1975, Appl. Phys. Lett. **26**, 452.
Nishikawa, K., 1968, J. Phys. Soc. Jpn. **24**, 916.
Nishikawa, K., 1968, J. Phys. Soc. Jpn. **24**, 1152.
Pantell, R. H., G. Soncini, and H. E. Puthoff, 1968, IEEE J. Quantum Electron. **QE-4**, 905.
Parsons, F. G., E. Yi-Chen, and R. K. Chang, 1971, Phys. Rev. Lett. **27**, 1436.
Patel, C. K. N., and R. E. Slusher, 1967, Phys. Rev. Lett. **19**, 1019.
Patel, C. K. N., and R. E. Slusher, 1968, Phys. Rev. Lett. **20**, 1087.
Patel, C. K. N., and V. T. Nguyen, 1969, Appl. Phys. Lett. **15**, 189.
Patel, C. K. N., and E. D. Shaw, 1970, Phys. Rev. Lett. **24**, 451.
Patel, C. K. N., and E. D. Shaw, 1971, Phys. Rev. B **3**, 1279.
Patel, C. K. N., 1972, Phys. Rev. Lett. **28**, 649.
Penn, D. R., 1962, Phys. Rev. **128**, 2093.
Phillips, J. C., 1968, Phys. Rev. Lett. **20**, 550.
Phillips, J. C., 1968, Phys. Rev. **166**, 832.
Phillips, J. C., 1968, Phys. Rev. **168**, 905.
Phillips, J. C., 1969, *Covalent Bonding in Crystals, Molecules, and Polymers* (University of Chicago, Chicago).
Phillips, J. C., 1973, *Bonds and Bands in Semiconductors* (Academic, New York).
Piestrup, M. A., R. N. Fleming, and R. H. Pantell, 1975, Appl. Phys. Lett. **26**, 418.
Pilipetskii, N. F., and A. R. Rustamov, 1965, Zh. Eksp. Teor. Fiz. Pis'ma Red. **2**, 88 [JETP Lett. **2**, 55 (1965)].
Popescu, D., C. B. Collins, B. W. Johnson, and I. Popescu, 1974, Phys. Rev. A **9**, 1182.
Porkolab, M., V. Arunasalam, and R. A. Ellis, 1972, Phys. Rev. Lett. **29**, 1438.
Rabi, I. I., 1937, Phys. Rev. **51**, 652.
Raizer, Yu. P., 1965, Usp. Fiz. Nauk. **87**, 29 [Sov. Phys.—Usp. **8**, 650 (1965)].
Ramsden, S. A., and W. E. R. Davis, 1964, Phys. Rev. Lett. **13**, 227.
Rao, D. V. G. L. N., and D. K. Aggarwal, 1971, Phys. Lett. A **37**, 383.
Rao, D. V. G. L. N., and S. Jayaraman, 1973, Appl. Phys. Lett. **23**, 539.
Régnier, F. R., and J. P-E. Taran, 1973, Appl. Phys. Lett. **23**, 240.
Rhodes, C. K., A. Szöke, and A. Javan, 1968, Phys. Rev. Lett. **21**, 1151.
Rhodes, C. K., and A. Szöke, 1969, Phys. Rev. **184**, 25.
Ripin, B. H., J. M. McMahon, E. A. McLean, W. M. Manheimer, and J. A. Stamper, 1974, Phys. Rev. Lett. **33**, 634.
Roberts, D. E., and E. N. Fortson, 1973, Phys. Rev. Lett. **31**, 1539.
Robinson, F. N. H., 1967, Bell Syst. Tech. J. **46**, 913.
Robinson, F. N. H., 1968, J. Phys. C **1**, 286.
Rosenbluth, M. N., 1972, Phys. Rev. Lett. **29**, 565.
Rosenbluth, M. N., and C. S. Liu, 1972, Phys. Rev. Lett. **29**, 701.
Rubenstein, J., 1970, J. Math. Phys. **11**, 258.
Rudnick, J., and E. A. Stern, 1971, Phys. Rev. B **4**, 4274.
Sacchi, C. A., C. H. Townes, and J. R. Lifshitz, 1968, Phys. Rev. **174**, 439.
Salamo, G. J., H. M. Gibbs, and G. G. Churchill, 1974, Phys. Rev. Lett. **33**, 273.
Sattler, J. R., B. A. Weber, and J. Nemarich, 1974, Appl. Phys. Lett. **25**, 491.
Schlossberg, H. R., and A. Javan, 1966, Phys. Rev. **150**, 267; erratum: 1972, Phys. Rev. A **5**, 1974.
Schmidt, J., P. R. Berman, and R. G. Brewer, 1972, Phys. Rev. Lett. **31**, 1103.
Schmidt, J., P. R. Berman, and R. G. Brewer, 1973, Phys. Rev. Lett. **31**, 1103.
Schmidt, W., and W. Appt, 1974, in VIII International Quantum Electronics Conference (San Francisco), paper R. 6.
Scholl, F., and C. L. Tang, 1973, Phys. Rev. B **8**, 4607.
Shelton, J. W., and Y. R. Shen, 1970, Phys. Rev. Lett. **25**, 23.
Shelton, J. W., and Y. R. Shen, 1971, Phys. Rev. Lett. **26**, 538.
Shelton, J. W., and Y. R. Shen, 1972, Phys. Rev. A **5**, 1867.
Shen, Y. R., and N. Bloembergen, 1965, Phys. Rev. **137**, A1786.
Shen, Y. R., 1965, Phys. Rev. **138**, A1741.
Shen, Y. R., and Y. J. Shaham, 1965, Phys. Rev. Lett. **15**, 1008.
Shen, Y. R., and M. M. T. Loy, 1971, Phys. Rev. A **3**, 2099.
Shen, Y. R., 1973, Appl. Phys. Lett. **23**, 516.
Shen, Y. R., 1975, in *Raman Scattering in Solids*, edited by M. Cardona (Springer, Berlin).
Shimizu, F., and E. Courtens, 1971, in *Fundamental and Applied Laser Physics*, edited by M. S. Feld, A. Javan, and N. A. Kurnit (Wiley, New York), p. 6.
Shimizu, F., 1973, IBM J. Res. Dev. **17**, 286.
Shoemaker, R. L., and R. G. Brewer, 1972, Phys. Rev. Lett. **28**, 1430.
Silin, V. P., 1965, Zh. Eksp. Teor. Fiz. **48**, 1679 [Sov. Phys.—JETP **21**, 1127 (1965)].
Singh, S., 1971, in *Handbook of Lasers*, edited by R. J. Pressley (Chemical Rubber Co., Cleveland), p. 489.
Skribanowitz, N., I. P. Herman, J. C. MacGillivray, and M. S. Feld, 1973, Phys. Rev. Lett. **30**, 309.
Slusher, R. E., and H. M. Gibbs, 1972, Phys. Rev. A **5**, 1634; erratum: 1972, Phys. Rev. A **6**, 1225.
Slusher, R. E., 1974, in *Progress in Optics*, edited by E. Wolf (North-Holland, Amsterdam), Vol. 12.
Smith, D. C., 1971, Appl. Phys. Lett. **19**, 405.
Smith, R. A., 1972, in *Laser Handbook*, edited by F. T. Arecchi and E. O. Schulz-Dubois (North-Holland, Amsterdam), p. 837, and the references therein.
Smith, W. L., J. H. Bechtel, and N. Bloembergen, 1975, Phys. Rev. B **12**, 706.
Sorokin, P. P. and J. R. Lankard, 1973, IEEE J. Quantum Electron. **QE-9**, 227.
Sorokin, P. P., J. J. Wynne, and J. R. Lankard, 1973, Appl. Phys. Lett. **22**, 342.
Stafford, R. G., and M. Sonderfeld, 1974, Phys. Rev. B **10**, 3471.
Stolen, R. H., E. P. Ippen, and A. R. Tynes, 1972, Appl. Phys. Lett. **20**, 62.
Stolen, R. H., and E. P. Ippen, 1973, Appl. Phys. Lett. **22**, 276.
Stolen, R. H., and A. Ashkin, 1973, Appl. Phys. Lett. **22**, 294.
Stolen, R. H., J. E. Bjorkholm, and A. Ashkin, 1974, Appl. Phys. Lett. **24**, 308.
Stolen, R. H., 1975, IEEE J. Quantum Electron. **QE-11**, 100.
Stone, J., 1975, Appl. Phys. Lett. **26**, 163.
Suematsu, Y., Y. Sasaki, and K. Shibata, 1973, Appl. Phys. Lett. **23**, 137.
Suematsu, Y., Y. Sasaki, K. Furuya, K. Shibata, and S. Ibu-

kuro, 1974, IEEE J. Quantum Electron. **QE-10**, 222.
Sukhamte, V. P., and P. A. Wolff, 1974, IEEE J. Quantum Electron. **10**, 870.
Svelto, O., 1974, in *Progress in Optics*, edited by E. Wolf (North-Holland, Amsterdam), Vol. XII.
Szabo, A., 1970, Phys. Rev. Lett. **25**, 924.
Szöke, A., and A. Javan, 1963, Phys. Rev. Lett. **10**, 521.
Szöke, A., 1964, Bull. Am. Phys. Soc. **9**, 490.
Talanov, V. I., 1964, Izv. Vyssh. Uchebn. Zaved. Radiofiz. **7**, 564.
Talanov, V. I., 1965, Zh. Eksp. Teor. Fiz. Pis'ma Red. **2**, 218 [JETP Lett. **2**, 138 (1965)].
Tang, C. L., and H. Statz, 1968, Appl. Phys. Lett. **10**, 145.
Tang, C. L., and C. Flytzanis, 1971, Phys. Rev. B **4**, 2520.
Tang, C. L., 1973, IEEE J. Quantum Electron. **QE-9**, 755.
Tan-no, N., and K. Yokoto, 1972, Phys. Rev. Lett. **29**, 1211.
Tan-no, N., T. Shirahata, K. Yokoto, and H. Inaba, 1975, Phys. Rev. A **11**, 159.
Thompson, D., and P. D. Coleman, 1974, reported by A. L. Robinson in Science **184**, 1064.
Tien, P. K., R. Ulrich, and R. J. Martin, 1970, Appl. Phys. Lett. **17**, 447.
Tien, P. K., 1971, Appl. Opt. **10**, 2395.
Treacy, E. B., 1968, Phys. Lett. **27A**, 421.
Treacy, E. B., and A. J. DeMaria, 1969, Phys. Lett. **29A**, 369.
Tsytovich, V. N., 1970, *Nonlinear Effects in Plasmas* (Plenum, New York).
Tuccio, S. A., J. W. Dubrin, O. G. Peterson, and B. B. Snavely, 1974, VIII International Quantum Electronics Conference (San Francisco), post-deadline paper Q.14.
van der Ziel, J. P., R. C. Miller, R. A. Logan, W. A. Nordland, and R. M. Mikulyak, 1974, Appl. Phys. Lett. **25**, 238.
Vasilenko, L. S., V. P. Chebotaev, and A. V. Shishaev, 1970, Zh. Eksp. Teor. Fiz. Pis'ma Red. **12**, 161 [JETP Lett. **12**, 113 (1970)].
von der Linde, D., A. Laubereau, and W. Kaiser, 1971, Phys. Rev. Lett. **26**, 954.
Voronov, G. S., V. M. Gorbunkov, G. A. Delone, N. B. Delone, L. V. Keldysh, O. V. Kudrevatova, and M. S. Rabinovich, 1966, Proceedings of the 8th International Conference on Phenomena in Ionized Gases (Beograd, Yugoslavia), edited by B. Perovic and D. Tosic (Gradevinska Kujiga Publ. House), Vol. 1, p. 806.
Voronov, G. S., 1966, Zh. Eksp. Teor. Fiz. **51**, 1496 [Sov. Phys.—JETP **24**, 1009 (1967)].
Walter, J. P., and M. L. Cohen, 1971, Phys. Rev. Lett. **26**, 17.
Wang, C. C., 1966, Phys. Rev. Lett. **16**, 344.
Wang, C. C., 1966, Phys. Rev. Lett. **152**, 149.
Wang, C. C., 1966, J. Appl. Phys. **37**, 1943.
Wang, C. C., and L. I. Davis, 1971, Phys. Rev. Lett. **26**, 822.
Wang, C. C., and L. I. Davis, 1973, Opt. Commun. **7**, 61.
Weiss, W. L., M. W. Smith, and B. M. Miles, 1969, National Bureau of Standards Report NSRDA-NBS 22.
Wong, G. K. L., and Y. R. Shen, 1972, Appl. Phys. Lett. **21**, 163.
Wong, G. K. L., and Y. R. Shen, 1973, Phys. Rev. Lett. **30**, 895.
Wong, G. K. L., and Y. R. Shen, 1974, Phys. Rev. Lett. **32**, 527.
Wong, G. K. L., and Y. R. Shen, 1974, Phys. Rev. A **10**, 1277.
Worlock, J. M., 1972, in *Laser Handbook*, edited by F. T. Arecchi and E. O. Schulz-Dubois (North-Holland, Amsterdam), p. 1323.
Wynne, J. J., 1972, Phys. Rev. Lett. **29**, 650.
Wynne, J. J., 1972, Phys. Rev. B **6**, 534.
Wynne, J. J., P. P. Sorokin, and J. R. Lankard, 1973, in *Proceedings of the Laser Spectroscopy Conference*, edited by R. G. Brewer and A. Mooradian (Plenum, New York, 1974).
Yablonovitch, E., 1971, Appl. Phys. Lett. **19**, 495.
Yablonovitch, E., and N. Bloembergen, 1972, Phys. Rev. Lett. **29**, 907.
Yablonovitch, E., C. Flytzanis, and N. Bloembergen, 1972, Phys. Rev. Lett. **29**, 865.
Yablonovitch, E., 1973, Appl. Phys. Lett. **23**, 121.
Yablonovitch, E., 1973, Phys. Rev. Lett. **31**, 877.
Yablonovitch, E., 1974, Phys. Rev. Lett. **32**, 1101.
Yablonovitch, E., 1974, Phys. Rev. A **10**, 1888.
Yajima, T., and K. Inoue, 1968, IEEE J. Quantum Electron. **QE-4**, 319.
Yajima, T., and K. Inoue, 1968, Phys. Lett. **26A**, 281.
Yajima, T., and K. Inoue, 1969, IEEE J. Quantum Electron. **QE-5**, 140.
Yamanaka, C., T. Hamanaka, T. Sasaki, J. Mizui, and H. B. Kang, 1974, Phys. Rev. Lett. **32**, 1038.
Yamanaka, C., T. Yamanaka, J. Mizui, and N. Yamaguchi, 1975, Phys. Rev. A **11**, 2138.
Yang, K. H., J. R. Morris, P. L. Richards, and Y. R. Shen, 1973, Appl. Phys. Lett. **23**, 669.
Yarborough, J. M., S. S. Sussman, H. E. Puthoff, R. H. Pantell, and B. C. Johnson, 1969, Appl. Phys. Lett. **15**, 102.
Young, J. F., G. C. Bjorklund, A. H. Kung, R. B. Miles, and S. E. Harris, 1971, Phys. Rev. Lett. **27**, 1551.
Zembrod, A., and Th. Gruhl, 1971, Phys. Rev. Lett. **27**, 287.
Zemon, S., R. R. Alfano, S. L. Shapiro, and E. Conwell, 1972, Appl. Phys. Lett. **21**, 327.
Zernike, F., and J. E. Midwinter, 1973, *Applied Nonlinear Optics* (Wiley, New York).
Zolotov, E. M., V. A. Kiselev, and V. A. Sychugov, 1974, Usp. Fiz. Nauk **112**, 231 [Sov. Phys.—Usp. **17**, 64 (1974)].

CONFERENCE PROCEEDINGS AND REVIEW BOOKS

Arecchi, F. T., and E. O. Schulz-Dubois, editors (1972), *Handbook of Lasers* (North-Holland, Amsterdam).
Brewer, R. G., and A. Mooradian, editors (1974), *Laser Spectroscopy* (Plenum, New York).
Feld, M. S., A. Javan, and N. A. Kurnit, editors (1973), *Fundamental and Applied Laser Physics* (Wiley, New York).
Glauber, R. G., editor (1969), *Quantum Optics* (Academic, New York).
Goodwin, D. W., editor (1970), *Advances in Quantum Electronics* (Academic, New York).
Grivet, P., and N. Bloembergen, editors (1964), *Quantum Electronics III* (Columbia University, New York).
Jacobs, S., M. Sargent, and M. O. Scully, editors (1974), *High Energy Lasers and Their Applications* (Addison-Wesley, Reading, Mass.).
Jacobs, S. F., M. Sargent, J. F. Scott, and M. O. Scully, editors (1975), *Laser Applications to Optics and Spectroscopy* (Addison-Wesley, Reading, Mass.).
Kelley, P. L., B. Lax, and P. E. Tannenwald, editors (1966), *Physics of Quantum Electronics* (McGraw-Hill, New York).
Mandel, L. and E. Wolf, editors (1972), *Coherence and Quantum Optics* (Plenum, New York).
Sanders, J. H., and S. Stenholm, editors (1969), *Progress in Quantum Electronics* (Pergamon, New York).
Schwarz, H. J., and H. Hora, editors (1969, 1971, 1973), *Laser Interaction and Related Plasma Phenomena* (Plenum, New York), Vols. I, II, and III.
Wolf, E., editor (1961), *Progress in Optics* (North-Holland, Amsterdam).
Yamanaka, C., and H. J. Schwarz, editors (1973), *Laser Interaction with Matter* (Japan Soc. for Promotion of Science, Tokyo).