From the current literature

NEW RESULTS ON THE RADIATION PROPERTIES OF OPTICAL MASERS (LASERS)

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A. Nonlinear effects. It is well-known that light scattered coherently in the visible and ultraviolet regions of the spectrum does not exhibit harmonics or "combination tones." In the language of classical physics this result is explained by the fact that the electric fields associated with the light wave are too weak to cause nonlinear deformation of the atoms or molecules responsible for the electronic part of the polarizability; this was the case for the highest intensities that were available until very recently. The relation between the electronic polarizability and the field intensity can generally be written as a power series which, for the present purposes, can be given in the form

$$P = \chi E \left(1 + \frac{E}{E_1} + \frac{E^2}{E_2^2} + \cdots \right),$$

where E is the intensity of the electric field associated with the light wave while E_1, E_2, ... are parameters of the order of magnitude of the atomic electric fields (approximately 10^8 cgs esu). It is thus clear that the quadratic or higher terms in E can be of importance only in external fields of extraordinary magnitude; until the present time such fields would have been unthinkable. If the light intensity corresponding to fields of this magnitude were obtained in the visible or ultraviolet portion of the spectrum one would expect to observe "overtones" and "optical beats" similar to those observed in nonlinear acoustic phenomena.

Fields of the required magnitude can, in fact, be realized in the monochromatic radiation produced by lasers. For instance, the ruby laser produces radiation at a wavelength of 6943 Å; when focused this radiation produces a field of the order of 10^5 V/cm. Hence, in principle, by using radiation from lasers it should be possible to observe nonlinear optical effects.

To observe these effects in practice, however, it is first necessary to overcome limitations due to the properties of the medium. It is obvious that the medium must be transparent for both the fundamental radiation and its harmonics. This condition is not sufficient, however. For example, examination of the polarization-tensor properties shows that the quadratic term in E in the polarization expression vanishes in an isotropic medium (glass) and in certain cases of point symmetry in a crystalline medium (the existence of a center of inversion). Crystalline quartz is found to be a suitable material for the observation of

nonlinear optical effects. Crystalline quartz was first used in experiments reported by P. A. Franken and his co-workers [1,2] at the University of Michigan. These workers observed the first harmonic of the radiation of a ruby laser, which was focused at a point inside the crystalline quartz. The output beam was analyzed with a spectrograph and it was found that the spectrum contained a second harmonic at $\lambda = 3472$ Å in addition to radiation at $\lambda = 6943$ Å.

"Sum" terms have been observed in another series of experiments. In this case use was made of the fact that the wavelength radiated by the ruby laser depends to some extent on its temperature. Specifically, two lasers, one at room temperature and the other at liquid-nitrogen temperature, radiate at wavelengths differing by approximately 10 Å. In [2] the pulsed excitation lamps of the two lasers were triggered by the same voltage pulse. The radiation of the two lasers was mixed by means of a half-silvered mirror and focused by means of a lens on the surface of a triglycine sulfate crystal, which was found to be more suitable than quartz for these experiments. The output radiation was analyzed with a quartz spectrograph. Under these conditions the spectrum exhibits three lines near 3470 Å: the outside lines correspond to harmonics of the cold laser and hot laser, and the center line corresponds to the sum of the frequencies of the two lasers (Fig. 1).

Nonlinear mixing of optical beams in crystals is the basis for other interesting effects. [3,4] Consider a plane monochromatic light wave $\exp[i(\omega_1 t - \mathbf{k}_1 \cdot \mathbf{r})]$. If it is of sufficient intensity this plane wave will produce a traveling plane wave of polarization in an appropriate nonlinear medium; this second wave will propagate with the same velocity as the exciting light wave. This means that the polarization term quadratic in E corresponds to a plane wave of polarization
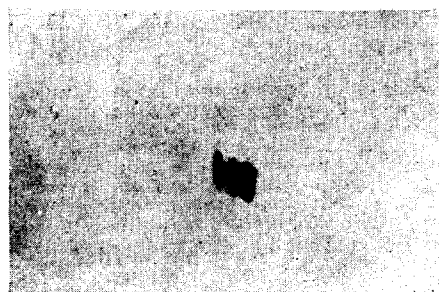

FIG. 1

$\exp[i(2\omega_1 t - 2\mathbf{k}_1 \cdot \mathbf{r})]$. In turn, this polarization wave produces a light wave—a harmonic at frequency ω_2 = $2\omega_1$. The highest efficiency obtains when both waves remain in phase i.e., when $\mathbf{k}_2 = 2\mathbf{k}_1$. But this means that the phase velocities of (ω/k) are equal, $v_1 = v_2$, so that the refractive index must be the same for both waves, $n_1 = n_2$. In the optical region, however, dispersion is almost always normal and $n_1 \neq n_2$; consequently the wave associated with the optical harmonic does not remain in step with the polarization wave.

There are, however, certain directions in an anisotropic crystal for which the phase velocities v_1 and v_2 are equal. In an anisotropic crystal the waves $\mathbf{k}_1$ and $\mathbf{k}_2$ each have two refractive indices n_e and n_0, associated with the ordinary and extraordinary waves. The discussion given in the original communication[3] shows that in the directions for which $v_1 = v_2$ the wave normal surfaces form a cone relative to the optical axis; the half angle of the cone is designated by ψ_0. In a uniaxial crystal a wave $\mathbf{k}_1$ produces a wave in phase with itself (a harmonic) only when $\mathbf{k}_1$ forms the angle ψ_0 with respect to the axis.

The experiment was carried out with a potassium dihydrogen phosphate crystal, which was illuminated by a parallel beam of light from a ruby laser ($\lambda = 6940$). After traversing the crystal the light passed through an ultraviolet filter that suppressed the radiation at the fundamental wavelength ($\lambda = 6940$) and transmitted only the radiation at the first harmonic $\lambda = 7347$ Å. A quartz lens focused this radiation on a photographic film on which was obtained a trace of the cross section of the light cone mentioned above. The angle ($\psi_0 = 49.8 + 1°$) determined experimentally from the geometry was found to be in good agreement with the calculated value $50.4°$.

Another experiment is based on the difference in phase velocity of light at the fundamental frequency (red $\mathbf{k}_r$) and the first harmonic (blue $\mathbf{k}_b$). After transmission in the forward direction through a crystal of thickness x the intensity of the blue light is

$$S = 2\pi c P^2 \left(\frac{k_b}{\Delta k}\right) \sin^2 \Delta kx, \qquad \Delta k = k_b - 2k_r.$$

Here, P is the magnitude of the induced blue polarization while k_b and k_r are the wave vectors corresponding to the blue and red light respectively. The factor $\sin^2 \Delta kx$ represents the dephasing between the red radiation (and correspondingly the blue polarization) and the blue radiation; this dephasing is due to the dispersion in the crystal, as explained above.

Thus, as the thickness of the crystal layer through which the red laser light passes is increased the intensity of the blue light leaving the crystal changes periodically in accordance with the factor $\sin^2 \Delta kx$. This effect was demonstrated with a quartz crystal. The light beam from a ruby laser was transmitted through a plane-parallel quartz plate. After passing through the crystal the red light was filtered by a solution of $CuSO_4$ and the transmitted light was monochromatized further by means of a grating monochromator. The optical thickness was changed by rotating the crystal about its axis.

The intensity of the transmitted blue light was measured with a photoelectric device. The curve obtained exhibits a periodic repetition of maxima and minima. As is evident from Fig. 2, the distance between successive maxima is in good agreement with that calculated from theory.

The dispersion in a potassium dihydrogen phosphate crystal can be compensated for. This crystal exhibits birefringence and the exciting ordinary ray (0) produces a first-harmonic extraordinary ray (e). Since the birefringence effect in this crystal is greater than the dispersion there is an orientation for which k_{be} is exactly equal to $2k_{ro}$. Under these conditions both rays remain in phase and the intensity of the blue light can be increased by a factor of 300.

B. Stimulated emission of organic molecules. Until very recently masers have made use of inorganic crystals with impurities (such as the ions Cr^{+++} or UO_2^+) or gases (helium-neon cw laser). With the appearance of the first work on lasers, however, attention was directed to the possibility of obtaining stimulated emission in the optical region of the spectrum by means of molecular crystals containing organic molecules.[5,6] In the first discussions of the problem it was pointed out that organic compounds with conjugate bonds have triplet metastable levels that are favorable for population inversion (negative absolute temperatures). We may recall a typical level scheme for such a molecule: consider only the electronic levels, neglecting the vibration levels located above each electronic level (although the vibrational levels are of importance in producing the conditions required for negative temperatures). The ground state S is a singlet (Fig. 3) and above it there are a series of singlet levels (starting with the second level the electronic levels are not separated). In addition to these singlet levels there are a number of triplet levels with
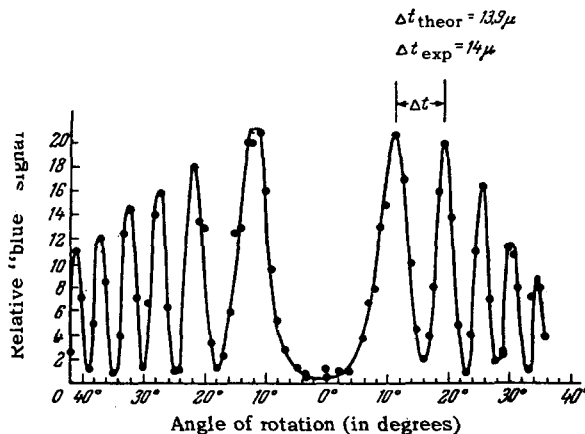

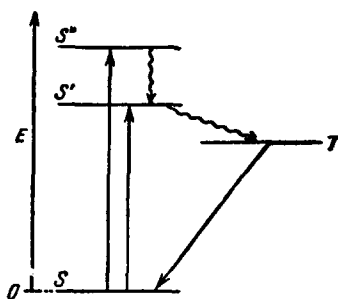Angle of rotation (in degrees)

FIG. 2

FIG. 3

FIG. 4

the lowest triplet level T located between the ground
singlet state and the first excited singlet state. The
molecule is excited to one of the electronic vibrational
levels S' or S". As a rule the first stage of the down-
ward transition is a radiationless transition (internal
conversion) to the lowest singlet pure electronic level.
Following this, transitions occur either with radiation
to an electronic vibrational level of the ground state
or, without radiation, to the lowest triplet level (cross-
ing). The transition from the T level to the ground
state S, an intercombination triplet-singlet transition,
is forbidden because the T level is metastable. The
possibility of a radiative transition (phosphorescence)
from this level to a lower level is due to the spin-orbit
interaction. The lifetime in the T level varies tremen-
dously (10^{-6} to 15 sec for different molecules). The
fact that the T level is metastable is favorable for pro-
ducing an excess population in this level with respect
to the lower level, thus providing the possibility of ob-
taining stimulated emission.

Rautian and Sobel'man[5] were apparently the first
to point out the feasibility of using organic systems for
producing an excess population in the excited level. A
similar suggestion was offered independently by the
Rochester group including Brock, Csavinszky, et al.[6]

A more complicated system has been used in an
organic-molecule laser[7] to produce a large excess
of molecules in the upper level (T) with respect to the
lower level (S); this system is described in a recently
published work. The authors indicate first of all the
use of a crystalline matrix of a so-called "rigid"
glass. The latter is a mixture of organic solvents
which yield a transparent glass upon solidification.
The possibility of using a glass matrix was indicated
in the gas laser of Javan, in which there was no or-
dered arrangement of the radiating molecules.

The organic system used by these authors is based
on energy transfer in the triplet level reported by
A. N. Terenin and V. L. Ermolaev.[8] This effect
consists of the transfer of energy of a molecule in
the excited triplet state to a molecule of another ma-
terial; the latter is excited to the triplet state directly,
thereby eliminating the usual preliminary transition
to a higher singlet state. Morantz, White, and Wright
(Woolwich Polytechnic Institute, London)[7] used the
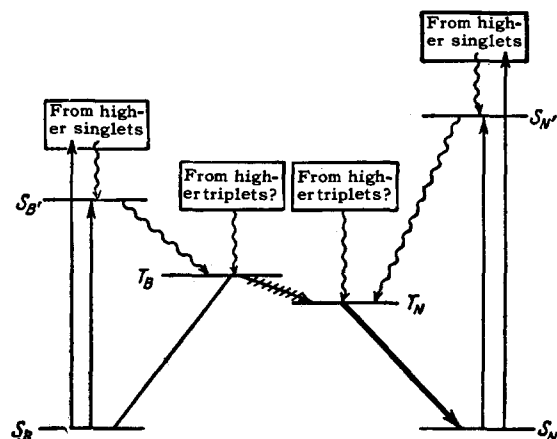system investigated by Terenin and Ermolaev—benzo-

phenone and naphthalene in a matrix of rigid glass
cooled to 77°K. The process can be understood from
an examination of Fig. 4. Mercury light $\lambda \sim 3650$ Å
is absorbed in the benzophenone but not the naphtha-
lene. Some of the benzophenone molecules make tran-
sitions to the metastable triplet state T_B as shown in
the diagram. The excitation energy is transferred to
the naphthalene molecule by radiationless transfer; the
napthalene triplet level T_N is somewhat below the T_B
level. Thus, the naphthalene molecule is excited to the
triplet state directly from the lowest singlet state by
virtue of energy transfer. The inverse process T_N
$\rightarrow S_N$ is a radiative process. To obtain the maximum
possible population in the T level the authors illumi-
nate the system with an intense flash of unfiltered light
containing ultraviolet. The T_N level is then populated
by virtue of the naphthalene as well as the triplet level
in the benzophenone (cf. Fig. 4). The frozen solution
(77°K), in the form of transparent glass, is located
between parallel reflection plates. The authors ob-
serve that at the critical illumination intensity the or-
dinary phosphorescence is replaced by an intense flash,
which is the induced coherent radiation. Positive ex-
perimental results were first obtained with benzophe-
none alone and then with the benzophenone-napthalene
system. Figure 5 shows oscillograms of the flashes in
this system.

The authors claim a number of advantages pos-
sessed by organic systems as compared with inorganic
systems. For example: 1) a large number of aromatic
compounds are capable of stimulated emission in vari-
ous parts of the visible spectrum, as well as the ultra-
violet and infrared, and the radiated frequencies can
be controlled by small modifications of the molecular
structure; 2) the relaxation time varies over wide lim-
its (from 10^{-4} to 10 sec).

The authors note that the use of glass matrices has
the advantage of considerable simplicity as compared
with crystalline matrices containing organic molecules.
It should be noted, however, that the system used by
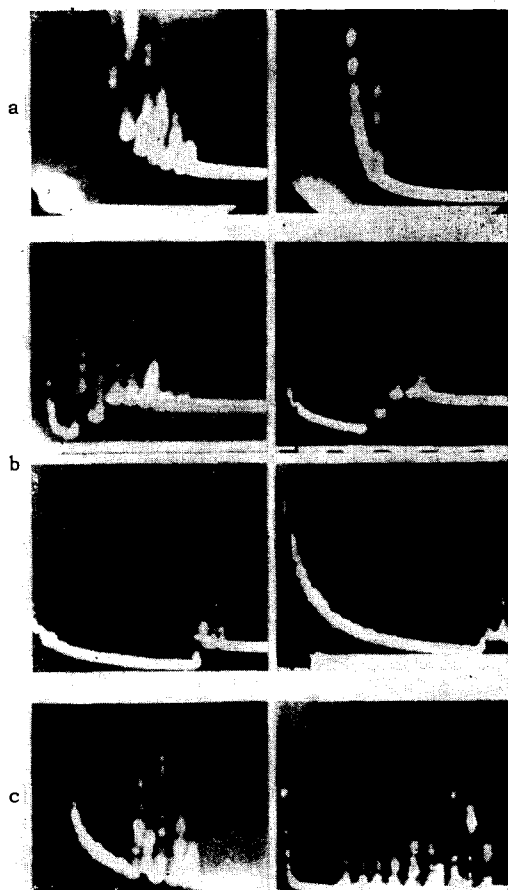these authors is not typical in all respects. One factor

FIG. 5. Oscillogram of the radiation. a) benzophenone;
b) and c) benzophenone plus naphthalene.

making for success in the experiment is the fact that the benzophenone spectrum consists of rather narrow bands; this is rarely the case, however, in frozen glass solutions.

[1] Franken, Hill, Peters, and Weinreich, Phys. Rev. Letters **7**, 118 (1961).

[2] Bass, Franken, Hill, Peters, and Weinreich, Phys. Rev. Letters **8**, 18 (1962).

[3] J. A. Giordmaine, Phys. Rev. Letters **8**, 19 (1962).

[4] Maker, Terhune, Niseiroff, and Savage, Phys. Rev. Letters **8**, 21 (1962).

[5] S. T. Rautian and I. I. Sobel'man, Opt. i spektr. (Optics and Spectroscopy) **10**, 134 (1961).

[6] Brock, Csavinszky, Hormats, Nedderman, Stirpe, and Unterleitner, J. Chem. Phys. **35**, 759 (1961).

[7] Morantz, White, and Wright, Phys. Rev. Letters **8**, 23 (1962).

[8] A. N. Terenin and V. L. Ermolaev, Sb. pamyati S. I. Vavilova (Memorial Volume to S. I. Vavilov) Acad. Sci. Press, 1952, p. 137.

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