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Detection of Weak Absorption Lines with the Aid of a Neodymium-Glass Laser

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A method is described for detection of weak absorption lines of gases whose absorption coefficients as low as 10^{-8} cm^{-1}. This method is based on multiple passage of light across an absorbing substance during laser action. It is shown that the gain of a laser with an inhomogeneously broadened gain profile remains constant throughout the frequency range of coherent emission. This ensures a high stability of the method. The theoretically predicted changes in the coherent emission spectra resulting from the presence of frequency-dependent losses in the resonator are confirmed by experimental results. The proposed method was used to study the absorption spectra of ammonia, acetylene, and water vapor in the 1.06 μ range.

THE distribution of intensity in the emission spectrum of a neodymium-glass laser is influenced strongly by the presence of frequency-dependent losses in the laser resonator.[1] In the present study this influence is used for detection of weak absorption lines.[2] We shall describe a study of the absorption of some gases in their transparency region near $\lambda = 1.06$ μ and we shall explain the reason for the high sensitivity of the proposed method.

1. DETECTION OF WEAK ABSORPTION

A layer of the gas under investigation was introduced into the resonator of a neodymium-glass laser. The influence of reflection from the surfaces of optical elements was eliminated by inclining all the surfaces at large angles (> 10°) with respect to the laser beam. The exceptionally weak absorption was investigated by reducing the pressure of the substance under study to $\sim 10^{-2}$ mm Hg. The absorption coefficients encountered in the present investigation were $\sim 10^{-8}$ cm^{-1} for gas layers 18 cm thick. The method employed enabled us to raise the sensitivity of the absorption analysis by at least two orders of magnitude. Figure 1 shows typical acetylene spectra obtained at various pressures. It is worth noting the periodic structure in these spectra (period 1.2 cm^{-1}), which corresponds to the rotational constant of acetylene. Departures from periodicity are due to superposition of several rotation-vibrational bands. The most likely participants are the vibrational bands at 8450 cm^{-1} (1, 1, 1), 9689 cm^{-1} (1, 2, 0), and 9835 cm^{-1} (3, 0, 0). When the pressure is reduced, the structure typical of the rotation-vibrational acetylene bands gradually disappears. This structure can be observed down to acetylene concentrations of ~ 10 $\sim 10^{-2}$ g/liter. All that remains below these concentrations is the structure due to absorption which is not associated with acetylene.

FIG. 1. Coherent emission spectrum of an Nd^{3+}-glass laser whose resonator included a layer of acetylene at various pressures: a) 1 atm; b) 0.5 atm; c) 0.1 atm.

FIG. 2. Cohereent radiation spectrum emitted by an Nd^{3+}-glass laser with a layer of water vapor (a) and a layer of air (b) in the resonator.

Only the molecules containing hydrogen have absorption bands in the emission region of the Nd^{3+}-glass laser ($\lambda_L = 1.06$ μ). The edges of the rotation-vibrational bands corresponding to the third harmonic of the R-H vibration lie in this range. It is very important to make an allowance for the absorption by water vapor, which is always present in air. Water has absorption bands in the region of 8807 cm^{-1} and 10613 cm^{-1}.[3] The edges of these bands can give rise to a structure in the laser emission region of Nd^{3+} ($\omega = 9434$ cm^{-1}). We investigated the absorption of water vapor in a layer 18 cm thick at t = 100°C and p = 760 mm Hg. Figure 2a shows the laser emission spectrum of Nd^{3+} in the presence of such a layer of water vapor. Figure 2b shows laser emission spectrum of Nd^{3+} obtained when a layer of atmospheric air, 50 cm thick, and of 60–70% humidity was inserted in the resonator. We can see that the characteristic bands due to the absorption by water vapor appear also when the laser radiation is generated in air. This point must always be allowed for in studies of the structure of the emission spectra of Nd^{3+}-glass lasers.

2. LINE STRUCTURE OF THE EMISSION SPECTRUM OF A LASER WITH AN INHOMOGENEOUSLY BROADENED GAIN PROFILE

The intensity distribution in the laser emission spectrum is highly sensitive to the absorption in the resonator because of the multiple passage of light through the absorbing substance. The absorption influences the emission spectrum if the gain $k(\omega)$ remains sufficiently constant throughout the emission spectrum. This can be achieved only in a laser with an inhomogeneously broadened gain profile, which results from the overlap of homogeneous profiles $g(\omega)$. The gain $k(\omega)$ is a function of the number of the active particles $N(\omega)$: $k(\omega) = \sigma N(\omega)$, where σ is the cross section for stimulated emission. The number of active particles capable of emitting light of frequency ω is governed by the rate of pumping and of de-excitation, i.e., by the rate of transition of particles from the upper level during laser emission. The radiation of frequency ω interacts with the particles whose spectrum lies within the homogeneous profile $g(\omega, \omega')$.

The rates of change in the number of the active particles and in the intensity of the radiation emitted by a laser with an inhomogeneously broadened gain profile is described by the equations:

$$\frac{dN(\omega,t)}{dt} = P - \frac{N(\omega,t)}{\tau} - N(\omega,t)c\tau\int_{-\infty}^{\infty} W(\omega' t)g(\omega,\omega')d\omega', \tag{1}$$

$$\frac{dW(\omega,t)}{dt} = W(\omega,t)c\sigma\int_{-\infty}^{\infty} N(\omega',t)g(\omega,\omega')d\omega' - \frac{W(\omega,t)}{T_{\text{ph}}(\omega)} + \rho(\omega). \tag{2}$$

In these equations $W(\omega, t)$ and $N(\omega, t)$ represent the spectral distributions of the numbers of photons and of active particles, respectively; T_{ph} is the frequency-dependent lifetime of a photon in the resonator; ρ is the spontaneous noise power expressed as the number of photons emitted in 1 cm^3 per 1 sec; P is the pumping power, expressed as the number of active particles generated in 1 cm^3 per 1 sec by the flashlamp radiation; τ is the lifetime of such particles under spontaneous radiation conditions; c is the velocity of light. These rate equations are derived on the assumption that the inhomogeneous width is infinite and that there is no migration of energy over the spectrum.

Let us consider the steady-state solutions of Eqs. (1) and (2). If $T_{\text{ph}}(\omega) \equiv T_0$, this solution is independent of ω and it yields the following values of the spectral radiation density and of the number of active particles, with a correction for spontaneous emission:

$$W_0 \approx T_0\left(P - \frac{1}{c\sigma\tau} + \rho\right) + \frac{\rho}{c\sigma\tau(P - 1/c\sigma\tau + \rho)}, \tag{3}$$

$$N_0 = 1/c\sigma T_0 - \rho/c\sigma W_0. \tag{4}$$

We shall now find the steady-state solution of Eqs. (1) and (2) in the case when the losses in the resonator depend on the frequency. We shall represent $1/T_{\text{ph}}(\omega)$ in the form

$$\frac{1}{T_{\text{ph}}(\omega)} = \frac{1}{T_0} - \Delta\left(\frac{1}{T_{\text{ph}}}\right)\cos(2\pi\omega/\Delta\omega) \tag{5}$$

and we shall seek $W(\omega)$ in the form

$$W(\omega) = W_0 + \Delta W\cos(2\pi\omega/\Delta\omega); \qquad \Delta W \ll W_0. \tag{6}$$

We shall assume that the homogeneously broadened line of a single ion has the dispersion profile of width γ:

$$g(\omega,\omega') = \frac{\gamma/2\pi}{(\omega-\omega')^2 + (\gamma/2)^2}. \tag{7}$$

Substituting Eqs. (6) and (7) into Eq. (1), we obtain the following expression for $N(\omega)$:

$$N(\omega) = N_0 - \frac{c\sigma N_0^2}{P}\Delta W e^{-\pi\gamma/\Delta\omega}\cos\frac{2\pi\omega}{\Delta\omega}. \tag{8}$$

It is evident from the above equation that the laser radiation spectrum has very little effect on the distribution of the number of the active particles $N(\omega)$ within a spectral interval $\Delta\omega$ which is small compared with the homogeneous width γ. The spectral distribution of the laser radiation $W(\omega)$ occurs in the expression for $N(\omega)$ only in the form of a product with an exponential factor $\exp(-\pi\gamma/\Delta\omega)$. The same factor has to be added to the gain:

$$k(\omega) = \sigma\int_{-\infty}^{\infty}\left(N_0 - \Delta N\cos\frac{2\pi\omega'}{\Delta\omega}\right)\frac{\gamma}{(\omega-\omega')^2+(\gamma/2)^2}\frac{d\omega'}{2\pi} \tag{9}$$
$$= k_0 - \sigma\Delta N e^{-\pi\gamma/\Delta\omega}\cos\frac{2\pi\omega}{\Delta\omega}.$$

The gain $k(\omega)$ will therefore be an even smoother function of the frequency, irrespective of the distribution of the radiation intensity in the spectral interval $\Delta\omega \ll \gamma$. For example, if $\gamma = 20\ \text{cm}^{-1}$ and $\Delta\omega = 1\ \text{cm}^{-1}$, we find that $\Delta k \sim e^{-120}$. In view of this high stability of the gain the distribution of the radiation intensity will be strongly affected even by weak frequency-dependent losses provided the photon lifetime in the resonator is long.

The relationship between ΔW and $\Delta(1/T_{\text{ph}})$ can be found from Eq. (1) with the aid of Eq. (8):

$$W_0\Delta\left(\frac{1}{T_{\text{ph}}}\right) = \left[\frac{\rho}{W_0} + \frac{c^2\sigma^2 W_0 P}{(c\sigma W_0 + 1/\tau)^2}e^{-2\pi\gamma/\Delta\omega}\right]\Delta W. \tag{10}$$

The relationship (10) can be transformed to a more convenient form if the correction for the spontaneous emission is ignored in Eq. (4) for N_0:

$$\frac{\Delta W}{W_0} = T_0\left(\frac{\rho T_0}{W_0} + \frac{W_0}{PT_0}e^{-2\pi\gamma/\Delta\omega}\right)^{-1}\Delta\left(\frac{1}{T_{\text{ph}}}\right). \tag{11}$$

The quantity $\rho T_0/W_0$ is the ratio of the spontaneous noise power to the laser radiation power and it is equal to the ratio of the number of photons emitted spontaneously into one mode to the number of stimulated photons generated per unit time. The quantity W_0/PT_0 is the ratio of the laser output power to the pumping power: this ratio is of the order of unity. Thus, if the laser resonator contains a substance whose absorption lines are of such width $\Delta\omega$ that

$$e^{-2\pi\gamma/\Delta\omega}W_0/PT_0 \ll \rho T_0/W_0, \tag{12}$$

a line structure will be observed in the laser emission spectrum even when the losses in the resonator change (because of absorption) by an amount as small as

$$T_0\Delta\left(\frac{1}{T_{\text{ph}}}\right) \sim \frac{\rho T_0}{W_0} \ll 10^{-7} - 10^{-9}.$$

This is why a laser with an inhomogeneously broadened gain profile can be used to detect weak absorption lines.

3. EXPERIMENTAL DETERMINATION OF THE SENSITIVITY OF THE PROPOSED METHOD

An experimental check of the theory of the formation of a structure in the emission spectrum of the Nd^{3+}-glass laser (Sec. 2) could be made provided carefully controlled frequency-dependent losses were introduced into the resonator. This could be done by inserting a Fabry-Perot interferometer with a controlled reflection coefficient in the resonator. The interferometer was formed by a plane-parallel layer of a liquid. This liquid was enclosed in a cuvette whose internal surfaces were parallel but external surfaces were inclined. The interference between light reflected from the internal surface made the transmission of the cuvette a function of the frequency:

$$A = A_0 + \Delta A\cos(2\pi\omega/\Omega),$$

where $\Omega = c/2Ln$; L is the thickness of the cuvette; n is the refractive index. The depth of modulation of the transmission, ΔA, was governed by the coefficient of reflection from the interface between the liquid and the cuvette wall. This coefficient could be varied by altering the composition of the liquid in the cuvette. The liquid employed was a mixture of benzene and chlorobenzene. The reflection coefficient could be var-

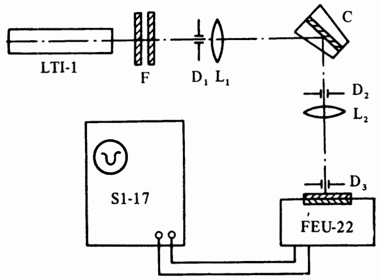

FIG. 3. Schematic diagram of the apparatus used to measure the reflection coefficient.

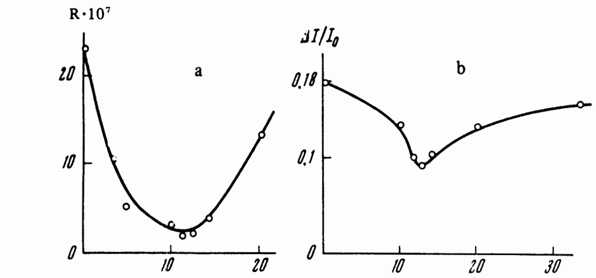

FIG. 4. Dependences of the reflection coefficient R (a) and of the depth of modulation of the laser emission spectrum (b) on the concentration of benzene in chlorobenzene.

ied from 10^{-5} to 10^{-7} by altering the concentration of benzene. Larger values of the reflection coefficient were obtained by utilizing the interface between glass and air (R = 0.04) and between glass and acetone.

The reflection coefficient was measured independently using the apparatus shown schematically in Fig. 3. The source of light was a laser in which the active medium was yttrium-aluminum garnet doped with Nd^{3+} ions ($\lambda_L = 1.06\ \mu$). Light from this laser (LTI-1 in Fig. 3) was attenuated with calibrated filters F and it reached a cuvette C via a system of lenses L and diaphragms D (the latter were used to eliminate scattered light). The light reflected from the cuvette was detected with an FÉU-22 photomultiplier and an S1-17 oscillograph. The reflection coefficient was measured to within 30% and this precision was obtained for values of R exceeding 2×10^{-7}. The dependence of the reflection coefficient on the concentration of benzene in chlorobenzene is plotted in Fig. 4a. A minimum of the reflection coefficient was observed at about 12% benzene and the value of the coefficient at this minimum did not exceed 2×10^{-7}. The sensitivity of our apparatus was too low and the thermal fluctuations of the refractive index too high for determination of smaller reflection coefficients. The cuvette was placed in the resonator of a laser whose active medium was Nd^{3+}-doped glass. The resonator of this laser was formed by special mirrors. In view of the high sensitivity of the laser emission spectrum to the frequency-dependent losses in the resonator it was necessary to eliminate all accidental selection. Consequently, the mirror bases were 3 cm thick and their rear surfaces were inclined at 10°. Therefore, only $\sim 10^{-6}$ of the light reflected from the rear surface of the mirror or $\sim 10^{-9}$ of the light incident on this surface (the reflection coefficient of the mirrors was 96%) was returned back to the resonator because of diffraction. At lower angles of inclination of the rear surfaces of the mirror the emission spectrum acquired a structure which was due to reflection of light from the surfaces of the mirror bases. The laser radiation was focused onto the slit of an STÉ-1 spectrograph and recorded on a photographic film.

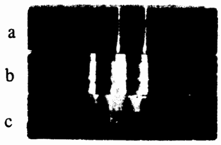

FIG. 5. Coherent radiation spectrum of an Nd^{3+}-glass laser at various temperatures: a) 290°K; b) 260°K; c) 240°K.

The laser radiation spectrum exhibited clearly a periodic structure which was due to the selective properties of the interferometer. The depth of modulation of this structure was a function of the reflection coefficient, i.e., of the concentration of benzene in chlorobenzene. Figure 4b shows the dependence of the depth of modulation on the concentration of benzene. When this concentration was 12%, the periodic structure was still clearly observed although the depth of modulation was minimal (10%). This situation corresponded to the minimum of the reflection coefficient whose value at this benzene concentration did not exceed 2×10^{-7}.

The sensitivity of the laser radiation spectrum to the presence of discrimination losses obeyed Eq. (11): it was an exponential function of the ratio $\Delta\omega/\gamma$ (the ratio of the transmission period $\Delta\omega$ to the homogeneous width γ). The homogeneous width of the gain profile of a single Nd^{3+} ion in glass decreased when the temperature was lowered and, therefore, the laser radiation spectrum should become smoother at lower temperatures. The first to disappear should be the large-scale structure with the period $\Delta\omega > \gamma$. Figure 5 shows the spectrum of the radiation emitted from a Nd^{3+}-glass laser at various temperatures. In this case the resonator contained a cuvette whose reflection coefficient was 10^{-5} and whose optical thickness was 0.025 cm, corresponding to $\Delta\omega = 20\ cm^{-1}$. We can see that when the temperature was lowered from 290 to 240°K the spectrum changed from discrete to continuous. This could explain the disappearance of the line structure in the laser radiation spectrum observed at liquid helium temperature.[4]

CONCLUSIONS

It should be stressed that the proposed method is suitable only for narrow absorption lines, i.e., in practice it can only be used for gases. If the line width is comparable with the homogeneous width, which is true of most cases of absorption in condensed media, the sensitivity of the method is much poorer. The absorption coefficients of gases measured in our study were 10^{-6} cm. Even weaker absorption lines could be detected by investigating the kinetics of laser emission and of transient effects in the distribution of the population inversion and the emitted radiation.

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239