The optoacoustic effect in methanol optically pumped by CO_2 laser*

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The optoacoustic effect has been obtained in gaseous methanol (CH_3OH) optically pumped by CO_2 laser. Theory of optoacoustic effect for simple two-level system is given.

1. Introduction

When modulated light beam illuminates an absorbant gas, it produces a sound wave in the gas. This is called optoacoustic effect and was discovered by Alexander Graham Bell in 1880 [1]. Optoacoustic experiments on gases were also performed by TYNDALL [2] and ROENTGEN [3], who had heard of Bell's discovery a year later. After the initial interest, experimentation with the optoacoustic effect apparently ceased. The experiments were difficult to perform and quantitate, since they required the investigator's ear to be the signal detector. Renewed interest in optoacoustic effect came back after the advent of microphone. In 1938 using the phenomenon VIENGEROV [4] began to study infrared light absorption in gases and to evaluate concentrations of gaseous species in gas mixtures. In 1946 GORELIK [5] proposed that a measurement of the optoacoustic signal phase could be used to investigate the rate of energy transfer between the vibrational and translational degrees of freedom of gas molecules. This proposal was successfully put into practice by SLOBODSKAYA [6]. Between 1950 and 1970 the optoacoustic effect was primarily employed to study vibrational lifetimes and other aspects of radiationless deexcitation in gases. In the early 1970's, after the advent of laser, optoacoustic effect attracted scientists' attention once again.

In this work, we report about the experiments on the optoacoustic effect in the gaseous methanol (CH_3OH). Cw CO_2 laser was used as the source of infrared radiation.

2. Theory

Let us consider a simple two-level energetic system for molecules of absorbant gas (Fig. 1). When a gas molecule absorbs a photon the molecule passes from its

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ground state E_0 to an excited state E_1. The molecule can then lose this energy and return to the ground state in the following ways [7]: (1) with photon reradiated, (2) with initiation of photochemical event, (3) with collision with another molecule of the same species that is in the ground state E_0 and excite it to its excited state E_1, and (4) with collision with any other molecule in the gas and transfer the energy to translational or kinetic energy shared by both molecules.
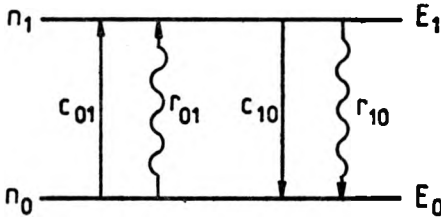

Fig. 1. Schematic representation of a two-level energetic system showing the radiative and nonradiative transitions

The sound wave detected by the microphone results from the fourth process, since an increased kinetic energy of the gas molecules is simply an increased temperature of the gas. If the incident photon radiation is intensity-modulated at a rate slower when compared with the rate of process (4) above, then the optical modulation results in a coherent modulation of the gaseous-sample temperature. From the gas laws it is clear that in the enclosed volume of the optoacoustic cell, the modulation of the gas temperature results in a periodic pressure fluctuation with a modulation frequency equal to the optical modulation one.

Let us consider the time dependence of n_1, the number of molecules per unit volume in energy state E_1. The rate of change of n_1 with time, dn_1/dt, is simple the number of molecules entering level 1 minus the number leaving it per unit time [7]. Thus

$$dn_1/dt = (r_{01} + c_{01})\,n_0 - (r_{10} + c_{10})\,n_1 \tag{1}$$

where r_{ij} – radiative transition rate from level i to level j,

c_{ij} – nonradiative collisionally-induced transition rate from E_i to E_j, clearly

$$r_{ij} = \varrho_\nu B_{ij} + A_{ij} \tag{2}$$

(where ϱ_ν – radiaton density at energy $E_\nu = h\nu = E_1 - E_0$, $B_{ij} = B_{ji}$ and it represents the Einstein coefficients for stimulated emission, and A_{ij} represents the Einstein coefficients for spontaneous emission). Thus in our model $A_{01} = 0$ since $E_1 > E_0$. It can be assumed that $c_{01} \simeq 0$, since there is a very low probability of a collisional excitation of an atom from the level 0 to the level 1 at room temperature. Thus

$$dn_1/dt = \varrho_\nu B_{10}(n_0 - n_1) - (A_{10} + c_{10})\,n_1 = \varrho_\nu B_{10}(n_0 - n_1) - (\tau_r^{-1} + \tau_0^{-1})\,n_1 \tag{3}$$

where $\tau_r = 1/A_{10}$ and $\tau_0 = 1/c_{10}$ are the respective relaxation times for radiative

and nonradiative/collisional transitions from the level 1. Defining a total relaxation time by τ, where

$$\tau^{-1} = \tau_r^{-1} + \tau_c^{-1}, \tag{4}$$

we obtain

$$dn_1/dt = \varrho_\nu B_{10}(n_0 - n_1) - \tau^{-1} n_1. \tag{5}$$

Similarly, for n_0

$$dn_0/dt = -\varrho_\nu B_{10}(n_0 - n_1) + \tau^{-1} n_1. \tag{6}$$

Thus

$$d/dt(n_1 - n_0) = -2\varrho_\nu B_{10}(n_1 - n_0) - 2\tau^{-1} n_1. \tag{7}$$

At steady state $d/dt(n_1 - n_0) = 0$. Thus

$$n_1 = \frac{\varrho_\nu B_{10} N}{2\varrho_\nu B_{10} + \tau^{-1}} \tag{8}$$

where $N = n_1 + n_0$ is the total number of molecules per cubic centimeter. Now, $\varrho_\nu = Ih\nu/c$, where I and c are the intensity and velocity of the light, respectively. Defining $B = B_{10}\,(h\nu/c)$, we obtain

$$n_1 = \frac{BIN}{2BI + \tau^{-1}}. \tag{9}$$

In the case, where the incident radiation is modulated at a frequency ω, we can set

$$I = I_0[1 + \delta \exp(i\omega t)], \; 0 \leqslant \delta \leqslant 1, \tag{10}$$

which gives

$$n_1 = N \frac{BI_0[1 + \delta \exp(i\omega t)]}{2BI_0[1 + \delta \exp(i\omega t)] + \tau^{-1}}. \tag{11}$$

When the excited molecules decay to the ground state by means of collision (the c_{ij} terms), the energy difference $\Delta E = E_1 - E_0$ passes into translational energy, that is, the velocities of the colliding molecules increase.

Ignoring the rotational and vibrational energies, the total internal energy of the gas per unit volume is given by [7]

$$U = \sum_i (n_i E_i) + K \tag{12}$$

where the sum is over all levels i, and K is the kinetic energy per cubic centi-

meter. In our simple model

$$U = n_1 E_1 + K \tag{13}$$

and

$$\frac{dU}{dt} = \frac{dn_1}{dt} E_1 + \frac{dK}{dt}. \tag{14}$$

Now, according to principle of energy conservation, dU/dt is simply equal to the difference between the energy absorbed and the energy reradiated. Thus

$$dU/dt = (r_{01}n_0 - r_{10}n_1)E_1, \tag{15}$$

and

$$dK/dt = c_{10}n_1 E_1. \tag{16}$$

From laws of thermodynamics, for constant volume, we have

$$dK = (\partial K/\partial T)_V dT = C_V dT \tag{17}$$

where T and V are the temperature and volume, respectively, and C_V is the specific heat per unit volume at constant volume. Therefore

$$K = C_V T + f(V) \tag{18}$$

where $f(V)$ is a volume-dependent function but independent of temperature. For an ideal gas, the pressure is given by

$$p = NkT \tag{19}$$

where k is the Boltzmann constant. Thus

$$p = kN \frac{K - f(V)}{C_V}. \tag{20}$$

The pressure wave is given by $\partial p/\partial t$. Taking the derivative of (20)

$$\frac{dp}{dt} = \frac{k}{C_V} N \frac{dK}{dt} = \frac{k}{C_V} N(c_{10}n_1 E_1). \tag{21}$$

Then, from (11) we have

$$\frac{dp}{dt} = \frac{k}{C_V} \frac{N^2 E_1}{\tau_0} \frac{BI_0[1 + \delta \exp(i\omega t)]}{2BI_0[1 + \delta \exp(i\omega t)] + \tau^{-1}}. \tag{22}$$

Expanding in powers series of $[\delta \exp(i\omega t)]$ and retaining only the $\exp(i\omega t)$ term,

we obtain

$$\frac{dp}{dt} = \frac{kE_1N^2}{C_V}\left\{\frac{2\tau_0^{-2}BI_0\delta}{(2BI_0+\tau^{-1})[(2BI_0+\tau^{-1})^2+\omega^2]^{1/2}}\right\}\exp\left[i(\omega t-\gamma)\right] \tag{23}$$

where $\gamma = \omega\tau$. Integration yields

$$p = \frac{kE_1N^2}{C_V\omega}\left\{\frac{2\tau_0^{-2}BI_0\delta}{(2BI_0+\tau^{-1})[(2BI_0+\tau^{-1})^2+\omega'^2]^{1/2}}\right\}\exp\left[i\left(\omega t-\gamma-\frac{\pi}{2}\right)\right]. \tag{24}$$

The optoacoustic microphone signal is proportional to p.

3. Experimental setup and results

The measurements were performed in the setup shown in Fig. 2. The CO_2 laser cavity was equipped with a plane reflecting diffraction grating, used to select laser lines in 9.4 μm band, and a concave ($R = 10$ m) germanium mirror on the piezoelectric transducer PZT. Two-section pyrex discharge tube, water-cooled, 120 cm long and 1.4 cm in diameter, was closed with NaCl Brewster-angle windows. The gas mixture of $CO_2 : N_2 : He$ at proportions of $1 : 1 : 4$ was used at
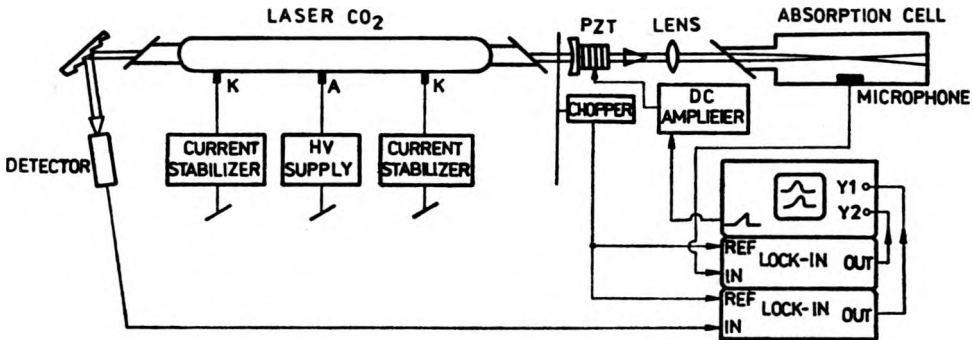

Fig. 2. Schematic diagram of the experimental set-up

an optimal total pressure of 13 Torr. The laser was operated with nonflowing gas at a stabilized discharge current of 12 mA for every section. The intensity of laser beam was modulated by means of the mechanical chopper at about 230 Hz. The absorption cell was evacuated and, next, filled with vapour of CH_3OH at pressure of 20 Torr. The cell was closed with NaCl window. The acoustic wave in the methanol was detected by a piezoelectric microphone and amplified by a lock-in technique. The profile of the laser gain curve was monitored with the piezoelectric detector from the grating side. Figure 3 shows 9P12, 9P14, 9P16 and 9P20 CO_2 emission lines and the corresponding optoacoustic signals.
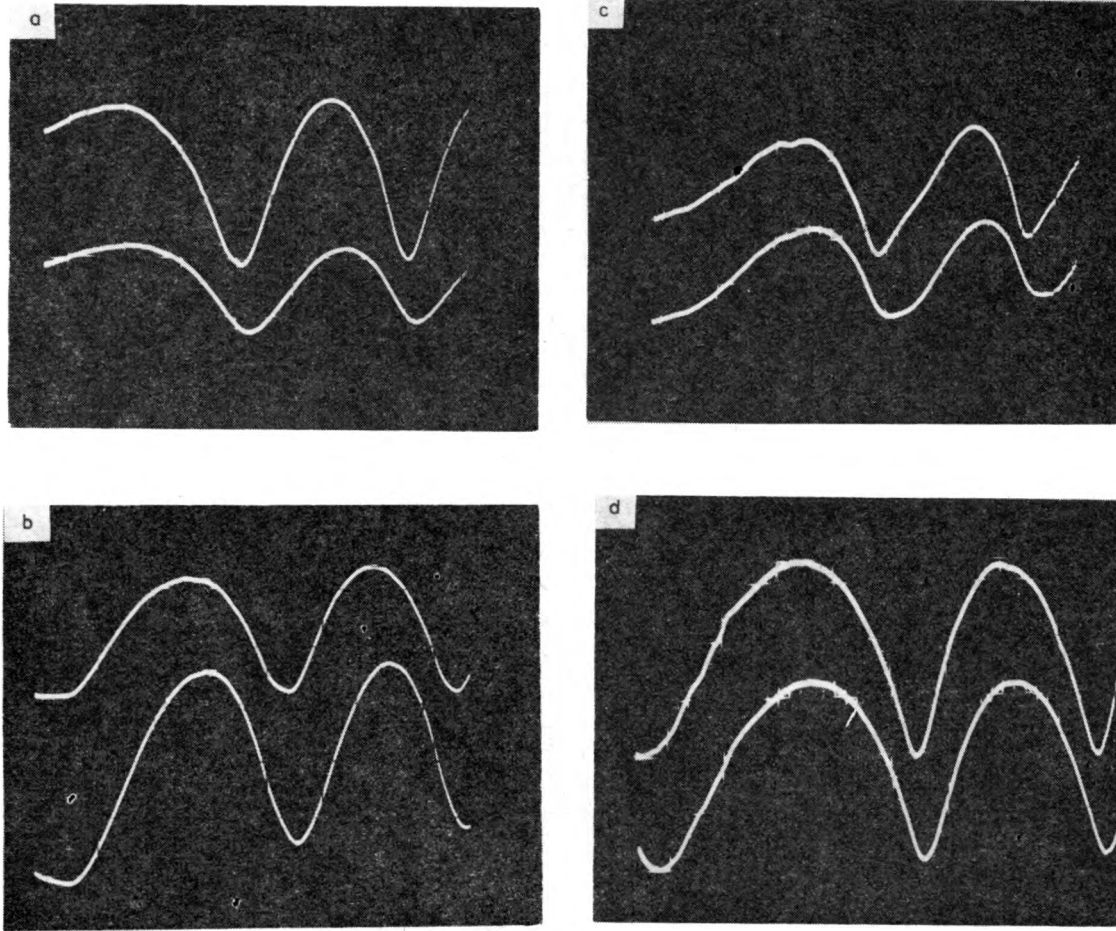
Fig. 3. Optoacoustic signal of CH_3OH (lower curves) as a function of the frequency detuning of the CO_2 9.3 µm-band lines (upper curves): 9P12 (a), 9P14 (b), 9P16 (c) and 9P20 (d)

4. Conclusion

In summary, we have demonstrated that there is an optoacoustic effect in methanol pumped optically by CO_2 laser. The optoacoustic signal is proportional to the intensity of infrared radiation coupled into cell. For this reason the optoacoustic effect can be used for far-infrared (FIR) lasers. For the operation of optically pumped FIR lasers, the pump laser must be set to the frequency at which the number of optically excited molecules is the greatest. This problem can be solved in a simple way by using the optoacoustic effect to monitor the number of optically excited molecules in the FIR laser cavity. What is only needed is to couple a microphone to the gas in the FIR laser resonator. When the modulated radiation of the pump laser is absorbed by the gas, periodic pressure changes occur due to the optoacoustic effect. The resulting acoustic signal is detected by a microphone. Hence, a microphone signal indicates the optical pumping and, thus, the microphone can be used as a sensing element in a feedback circuit, which stabilizes the pump laser frequency to the optimum pump frequency for FIR laser action.

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Исследование оптоакустического эффекта в метаноле, оптически накачиваемом CO_2 лазером

Сконстатирован оптоакустический эффект в паре метанола, оптически накачиваемом при помощи CO_2 лазера. Изложена теория оптоакустического эффекта для простой двухуровневой схемы.