HIGHLY SENSITIVE IR-SPECTROMETER/GAS ANALYZER IKS–GAZ

M.A. Merzlyakov

Novosibirsk State University

Received July 15, 1996

Based on general equations of hydrodynamics we describe the processes in a photoacoustic cell. The results of modeling a 1–D photoacoustic cell in computer simulations well agree with the experiment. Based on this effect we have developed a highly sensitive IR spectrometer/gasanalyzer "IKS-GASB having the threshold sensitivity at the level of 3 *by* 10^{-10} cm^{-1} *in the operation mode of a continuous flow of a sample under study. In the case of strongly absorbing gases (in the region* 9.2 *to* 10.8 μm*) that corresponds to their concentration of* 10^{-10} *percent by volume.*

INTRODUCTION

The opto-acoustic (OA) spectroscopy, with the use of lasers is increasingly used for analyzing the atmospheric gas composition due to its generality and high sensitivity.[1,2] Facilitation of the method potentialities faces some technical difficulties, e.g., radiation absorption in cell windows, noise influence etc. Earlier, we have proposed a Π-shaped OA-cell[3–7] that allows one to reduce the background noise from windows by a factor of 10^2–10^3 and place the cell within the laser cavity what makes it possible to operate in the regime of continuous flow of a sample analyzed, and provides a sharp increase in the sensitivity. The advantage is achieved owing to untraditional shape of the OA cell.

Complication of the shape and the change for higher modulation frequencies required a different approach to the calculation of the acoustic field in a cell. The change for resonant frequencies of an OA cell makes it important to take into account dissipative processes determined by the shape and dimensions of the cell. Another one feature of the given problem is the necessity of taking into consideration the complicated structure of the volume source of sound (it is determined by the intensity distribution over a laser beam) and significantly nonstationary character of the processes. The problem is solved by methods of gas dynamics, i.e., acoustics is considered as a particular case of the gas motion, and all the acoustic effects must follow from the general equations of hydrodynamics.

SIMULATION

The motion equations of a viscous compressible gas are very complicated. For this reason, only few problems have exact solutions. As a rule such problems are characterized by geometrical simplicity and certain symmetry conditions. As to the majority of other problems in viscous gas hydrodynamics, they are solved by approximate analytical methods or by numerical simulation.

The most general form of the equation of viscous gas motion is[8]

$$R\left[\frac{\partial v_i}{\partial \tau} + v_k \frac{\partial v_i}{\partial x_k}\right] = -\frac{\partial P}{\partial x_i} + $$

$$+\frac{\partial}{\partial x_k}\left\{\eta\left[\frac{\partial v_i}{\partial x_k}+\frac{\partial v_k}{\partial x_i}-\frac{2}{3}\delta_{ik}\frac{\partial v_l}{\partial x_l}\right]\right\}+\frac{\partial}{\partial x_i}\left[\zeta\frac{\partial v_l}{\partial x_l}\right], \quad (1)$$

where τ is time; η and ζ are coefficients of shift and volume viscosity; $R(\bar{r}, \tau)$, $P(\bar{r}, \tau)$, and $\bar{v}(\bar{r}, \tau)$ are gas density, pressure, and velocity at the point (x_1, x_2, x_3) and at the moment τ; i, k, l are vector and tensor indices (summation is meant by indices repeated twice), δ_{ik} is the unit tensor.

In most cases, the change of viscosity coefficients is insignificant and the equation (1) can be reduced to the Navier-Stokes equation. And if the viscosity is neglected completely (this is justified in some problems), we obtain

$$R\left[\frac{\partial \bar{v}}{\partial t} + (\bar{v}\nabla)\,\bar{v}\right] = -\operatorname{grad} P. \quad (2)$$

Since the oscillations in a sound wave are insignificant, the velocity $\bar{v}$ is small. So the term $(\bar{v}\nabla)\bar{v}$ can be neglected, and we obtain from Eq. (2)

$$R\,\frac{\partial \bar{v}}{\partial t} = -\operatorname{grad} P. \quad (3)$$

The principle of substance conservation for a compressible gas in hydrodynamics is expressed by the continuity equation

$$\frac{\partial R}{\partial t} + \operatorname{div} R\bar{v} = 0\ . \quad (4)$$

0235-6880/96/12 1057-04 $02.00

The energy conservation law takes the form

$$R\,\frac{\mathrm{d}W}{\mathrm{d}t} = \lambda\Delta T - P\ \mathrm{div}\ \bar{v} + \alpha'_{ik}\,\frac{\partial v_k}{\partial x_k} + Q(\bar{r},\ t)\ , \qquad (5)$$

where W is the density of the internal energy; α_{ik} is the viscous stress tensor; Q is the power density of heat sources; λ is the thermal conductivity, Δ denotes the operator ∇^2. When viscosity is absent, Eq. (5) takes the form

$$R\,\frac{\mathrm{d}W}{\mathrm{d}t} = \lambda\Delta T - P\ \mathrm{div}\ \bar{v} + Q(\bar{r},\ t)\ . \qquad (6)$$

To close the system, we add the equation of the gas state

$$P = P(R,\ T) \qquad (7)$$

and the expression for the internal energy of a gas

$$W = W(R,\ T)\ . \qquad (8)$$

Thus a non-viscous gas in a closed volume is described by the system of equations (3), (4), (6), (7), and (8), and the boundary conditions $T|_s = T_0$ and $v_\perp|_s = 0$, where T_0 is the temperature of walls.

At the first stage of work, a simplified model of thermooptical sound induction was chosen. We consider a one-dimensional case. The gas state is described by the equation $P = nkT$, where k is the Boltzmann constant. After writing explicitly the expression for the internal energy in the form $W = FkT/2$ (where F is the number of degrees of freedom giving a contribution into heat capacity), linearization near the state $Q = 0$:

$$T = T_0\ (1 + t),\quad R = R_0\ (1 + \rho),\quad W = W_0\ (1 + w),$$
$$P = P_0\ (1 + p)$$

and truncation of the series by neglecting the terms of second order of magnitude, we obtain

$$\frac{\partial\rho}{\partial\tau} = -\,\frac{\partial v}{\partial x}\,,\quad \frac{\partial v}{\partial\tau} = -\,\frac{P_0}{R_0}\frac{\partial\rho}{\partial x}\,,$$

$$\frac{\partial w}{\partial\tau} = \frac{\lambda}{R_0}\,\frac{T_0}{W_0}\,\frac{\partial^2 t}{\partial x^2} - \frac{P_0}{R_0W_0}\,\frac{\partial v}{\partial x} + \frac{Q_0}{R_0W_0}\,,$$

$$p = \rho + t\ ,\quad w = t\ ,\quad t(0,\ \tau) = 0\ ,\quad t(L,\ \tau) = 0\ ,$$
$$v(0,\ \tau) = 0\ ,\quad v(L,\ \tau) = 0\ .$$

To find a solution to the system, a program implementing the finite-difference method was created. The input parameters of the program are the length of the cell; temperature of the cell walls; gas heat conductivity; gas density in equilibrium conditions; mass of a gas molecule; degrees of freedom giving a contribution into the heat capacity; Boltzmann constant; distribution of density, temperature, and velocity at the initial moment; heat release function in space and time; calculation steps in time and space; frequency of the frame readout into a display and disk.

The program has no adjustment parameters. All the processes are completely determined by the above-mentioned input parameters. Each frame contains spatial distribution of heat release functions, gas flow velocity, temperature, and density. Current values of the functions are displayed and this enables us to analyze the results rapidly during the numerical experiment. There is a possibility to interrupt the numerical experiment (in this case, the current state is recorded onto the disk) and continue it at any time. The regime of scrolling earlier calculated data and recorded into a magnetic storage is also available.

We have simulated free oscillations of a gas disturbed from the equilibrium. The scrolling of calculated data has made it possible to identify the standing wave for which one wavelength (2nd harmonic of natural oscillations of the resonator) covers the whole cell length. The period of the 2nd harmonic of the model gas was determined by the time interval between frames. The sound velocity $C = 323$ m/s of the model gas was determined by the wavelength and period. This value well agrees with the reference data on real gases.

Strong attenuation of oscillations was observed with the increase of heat conductivity due to the growth of the dissipation processes.

Simulation of forced oscillations of the gas initiated thermooptical sound generation in an OA cell when the absorbing gas is illuminated with a laser beam modulated by amplitude. The form of the heat release function was chosen to be Gaussian with a maximum at the cell center, time modulation is the meander. We observed excitation of oscillations from the initially equilibrium conditions. Rapid increase in the velocity amplitude was recorded, the fourth harmonic was also excited to a noticeable level. Beats whose period was determined by detuning arose when the meander frequency did not coincide with the proper frequency of gas oscillations. The amplitude of forced oscillations decreased with the frequency increase (Fig. 1) and then it sharply increased near the resonance.

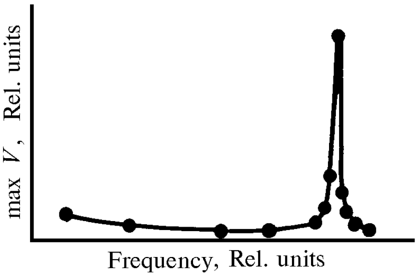

FIG. 1. Amplitude of gas velocity in a sound wave as a function of modulation frequency of radiation.

COMPARISON WITH THE EXPERIMENT

To check up the created model of thermooptical sound generation, we have arranged an experimental study of the phenomena. A П-shaped OA cell was filled with carbon dioxide and illuminated with amplitude-modulated laser radiation at 10.6 μm wavelength. The acoustic signal function of the modulation frequency is presented in Fig. 2.

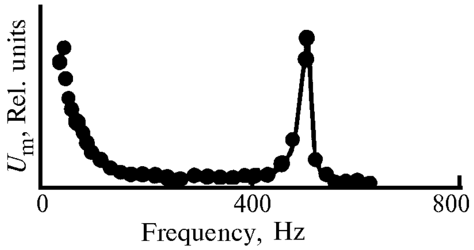

FIG. 2. The OA signal (U_m) as a *function of the modulation frequency.*

Since the possibilities for a comparison of the experimental results in a real 3-dimensional cell with numerical 1-dimensional experiment are restricted, we note some general regularities. In both cases, gas oscillations arise in a cell under the action of a periodic radiation. The amplitude of oscillations decreased with the frequency increase.

When the frequency of the exciting force approaches the frequency of natural oscillations of the cell, resonant amplification of the response is observed. The first resonance is observed at the sound wave length coinciding with the total length of the OA cell in both cases. Thus the model simulates effects observed experimentally, and the closeness of the calculated value of the sound velocity to the experimental one makes it possible to speak about a quantitative description of sound excitation due to the absorption of laser radiation.

INSTRUMENTATION

The IR spectrometer/Gas Analyzer IKS–GAZ consists of three units: optical module, power source ILGN–711, and an IBM PC compatible computer. The optical module (Fig .3) contains an active laser element *4* of the type ILGN–716 in which the input mirror is changed for a Brewster window. The diffraction grating *1* (100 grooves per mm) serves as a selective mirror. The angle of the grating inclination to the optical axis is driven with a stepper motor controlled with a computer *6*. Inside the resonator, a П-shaped OA cell *2* with a capacitor microphone *8* of the type M101 and a rotatable disk with slits *3* for radiation modulation are placed. The pyroelectric receiver *5* measures radiation power which significantly changes with the change of the laser generation wavelength.

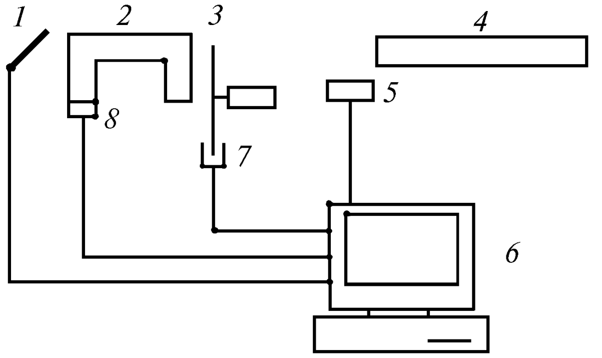

FIG. 3. Spectrometer scheme: 1 – diffraction grating; 2 – OA cell; 3 – modulator; 4 – laser tube; 5 – pyroelectrical receiver; 6 – computer; 7 – reference signal detector; 8 – microphone.

The discharge ignition in the laser tube generates IR radiation whose wavelength is determined by the angle of the diffraction grating. Generation at vibrational-rotational transitions of a CO_2 molecule is obtained (P- and R-arms in the ranges 00°1–10°0 and 00°1–02°0). Radiation is modulated by amplitude with the frequency coincident with the acoustic resonance of the OA cell. When the radiation is absorbed by a gas mixture, a standing sound wave is excited in the cell. The amplitude and phase of the wave are converted into an electrical signal U_m by the microphone. After analog-to-digital conversion, the signals from the microphone *8* and pyroelectric detector *5*, and the reference signal from the modulator *7* come into the computer *6* for the subsequent processing. The results of analysis are displayed in the form of a diagram and digital form, recorded on a magnetic disk, and printed out in a graphic or tabular form.

To determine the detection threshold in the continuous flow regime, a mixture of carbon dioxide with nitrogen entered to an OA cell under normal pressure and room temperature. Radiation was tuned at the P20 line of the transition 00°1–10°0 (the wavelength is 10.6 μm). The CO_2 content in N_2 was varied. The absorption by the mixture was estimated by CO_2 concentration and the absorption coefficient from Ref. 9. The limiting value of the detectable absorption coefficient turned to be $3 \cdot 10^{-10}$ cm^{-1}.

The dimensions of the optical module are 40×20×175 cm.

CONCLUSION

The developed mathematical model of sound generation by laser radiation takes into account the intensity distribution in a laser beam and completely describes the gas state evolution in a cell of an arbitrary shape and nonstationary processes. Comparison of test measurements and the data of numerical experiments with the one-dimensional variant of the model demonstrates that the model describes all the most important effects and well agrees with the experimental results.

The IKS–GAZ equipment permits one to measure IR absorption at generation lines of a CO_2 laser in the wavelength range 9.2...10.8 μm. The regime of measurements under continuous flow of a gas is realized. The limiting detectable absorption coefficient of $3\cdot10^{-10}$ cm^{-1} is achieved. For gases with strong absorption lines, IKS–GAZ makes it possible to perform efficient analysis of gas mixtures automatically and represent the results in the form easily entered onto a display or a printer. It is easy to integrate it into the measurement networks by standard facilities.

AKNOWLEDGMENTS

The work is partially supported by the Competition Center of the Fundamental Natural Science of Russian State Commitee on High Education in St. Petersburg State University (Grant No. 2–94–3–14).

REFERENCES

1. B.G. Ageev, T.P. Astafurova, Yu.N. Ponomarev, et al., Atmos. Oceanic Opt. **7**, No. 7, 528–530 (1994).
2. A. Thöny and M.W. Sigrist, Infrared Phys. Technol. **36**, 585–615 (1995).
3. M.A. Merzlyakov, in: *7th All-Union Symposium on Laser Radiation Propagation in the Atmosphere*, Tomsk, 1983.
4. M.A. Merzlyakov, “Otkrytiya i IzobreteniyaB, No. 13 (1983).
5. M.A. Merzlyakov, in: *Laser Application in Science and Technics. Proceedings of the IV All-Union Seminar*, Samara–Togliatti, 1991.
6. M.A. Merzlyakov, *The Second International seminar “Siberian Haze”*, Russia, Novosibirsk, 1993.
7. M.A. Merzlyakov, in: *Abstracts of Selected Works by Grants in Natural Sciences.* State Commitee of the Russian Federation on Higher Education, and the Competition Center of Fundamental Natural Sciences in St. Petersburg State University (St. Petersburg, 1994), pp. 104–105.
8. L.D. Landau and E.M. Lifshits, *Hydrodynamics* (Nauka, Moscow, 1986).
9. V.N. Aref'ev and N.I. Sizov, Kvant. Elektron. **4**, No. 6 (1977).