ON THE DEPENDENCE OF OPTO–ACOUSTIC DETECTOR SENSITIVITY ON PRESSURE OF A GAS UNDER STUDY

B.G. Ageev, O.Yu. Nikiforova, and V.A. Sapozhnikova

Institute of Atmospheric Optics,
Siberian Branch of the Russian Academy of Sciences, Tomsk
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Opto–acoustic detectors are widely used in laser gas analysis and spectroscopy. As a rule, these detectors are employed under atmospheric and, sometimes, under lower pressures. In this case the pressure dependence of opto–acoustic response appears. This paper describes the results of study of such dependences for H_2O, CO_2, *and their mixtures with different buffer gases with* CO_2*–laser radiation at* $\lambda = 10.6$ μm. *It was very interesting to compare the changes of photoacoustic amplitudes with pressure in these two gases because of specific behaviors of their absorption coefficients.*

It is well known that an opto–acoustic amplitude can be described by the Kerr––Atwood thermodynamic model,[1] when a weakly absorbing gas can be modeled as a solid body with some temperature change due to the absorption of the exciting laser radiation passing through it. Later, Wake and Amer[2] proposed using the Kerr––Atwood method the following expression for describing the opto–acoustic response due to absorption of a modulated radiation by a gas that included pressure–dependent sensitivity of a microphone:

$$U(P) = S(P, \overline{\gamma}, T)\, \kappa(P)\, \frac{PW}{4\pi \overline{k} T} \sum_m \frac{D_m \exp(i\theta_m)}{\sqrt{1 + \omega^2 a^4 / D^2 \xi_m^4}}, \qquad (1)$$

where W is the incident radiation power, κ is the absorption coefficient, a is the cell radius, P and T are the equilibrium pressure and temperature in the cell, ξ_m is the mth root of the zeroth–order Bessel function, $\overline{k}$ is the effective thermal conductivity, D is the effective thermal diffusivity of a gas or mixture, D_m are the numerically calculated coefficients, which depend on beam radius, S is the microphone sensitivity, and $\tan \theta_m = (\omega a^2 / D \xi_m^2)^{-1}$,

$$S(P, \overline{\gamma}, T) = S_0 \frac{1 + B}{1 + B(P, \overline{\gamma}, T_{STP}/\gamma_{air} TP)}, \qquad (2)$$

where $B \sim 1$, $\overline{\gamma} = (\overline{C}_v + R)/\overline{C}_v$, $\overline{C}_v = x_i C_{pi} + (1 - x_i) C_{pj} - R$, x is the molar fraction of the ith absorbing gas, j is for a buffer gas, C_{pi} and C_{pj} are the gas heat capacity of the absorbing and buffer gases, respectively. As can be seen from Eq. (2), the microphone sensitivity decreases with pressure.

Equation (1) can be rewritten in the form

$$U = \alpha\, \kappa\, W = S(P)\, \alpha'(P)\, \kappa(P)\, W, \qquad (3)$$

where α is the sensitivity of the opto–acoustic detector (OAD) which is proportional to the microphone sensitivity. The value

$$\alpha'(P) \cong \sum_m \frac{D_m \exp(i\theta_m)}{\sqrt{1 + \omega^2 a^4 / D^2 \xi_m^4}} \qquad (4)$$

describing the process of heat equilibrium reset in a gas, is independent of the microphone characteristics and tends to a constant value (depending on the beam radius) with pressure increase; the slope of $\alpha'(P)$ under small pressures depends on the thermal diffusivity of the absorbing gas or mixture.

Antipov et al.[3] proposed a model close to the expression from Ref. 2 for describing the OAD sensitivity.

$$\alpha = \text{const}\, \beta(P)\, \gamma(P)\, \varepsilon(P),$$

where $\beta(P)$ shows the efficiency of the absorbed energy transformation into the energy of translational motion of particles, $\gamma(P)$ relates the particle kinetic energy to the cell pressure increase, and $\varepsilon(P)$ is the membrane deflection when the acoustic signal appears in the cell and is proportional to the microphone sensitivity. In this case

$$\beta(P) = \frac{1}{1 + \tau_{VT}^0 / \tau_d^0 P^2}, \quad \gamma(P) = \frac{P\tau_T}{T r C_V \sqrt{1 + (\omega\tau_T)^2}},$$

$$\varepsilon(P) = \frac{\omega / a}{P + a / c_m},$$

where τ_{VT}^0 and τ_d^0 are the times of vibrational–translational relaxation and deactivation of the excited molecules on the cell walls under unit pressure, τ_T is the time of heat relaxation, T, ρ, and C_V are the temperature, density and heat capacity of the gas, ω is the frequency of modulation, c_m is the membrane flexibility, and a is the constant depending on the gas type.

Simultaneously with the procedure of calculating the microphone sensitivity $\varepsilon(P)$ the method of experimental recording of this dependence, i.e., the method of electrostatic activation has been proposed in Ref. 3. In this case, the pressure acting on the microphone membrane due to the opto–acoustic effect was imitated by the electrostatic attraction force. Application of this method to different absorbing gases, showed, as in Eq. (2), that the microphone sensitivity decreases with pressure increase.

We know few works in which the OAD sensitivity and its dependence on a gas mixture pressure, type of a buffer gas, and microphone characteristics were investigated in

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detail. In this paper we present the results of our investigation of the OAD sensitivity under different pressures for absorbing species H_2O, CO_2 and their mixtures with a buffer gas in the region of the CO_2 laser radiation at the wavelength $\lambda = 10.6$ μm and compare these results with those given in Refs. 2 and 3. The investigations have been carried out based on experiments (spectroscopic and model) and theoretical calculations for gases with the well–determined absorption coefficients for pure species and mixtures with buffer gases.[4,5]

The measurements were made with an OA spectrometer and a CO_2 tunable cw laser. The spectrometer was constructed using a traditional scheme (see, e.g., Ref. 6). The amplitude–modulated laser radiation (at frequency ≈ 90 Hz) passed through a 2–mm diaphragm into an OA detector cell, a custom–made OA–power meter was placed behind the cell. A home–made capacitor microphone was mounted on the cell wall ($\varnothing_{cell}$ = 10 mm and l = 250 mm). The microphone had an additional electrode–activator[3] for detecting the effect of gas pressure inside the cell on the mechanic impedance of a movable system of the microphone. An electrical signal from the microphone enters, through pre– and lock–in amplifiers, into a voltage converter, whose amplitude output is then recorded. Similar channel was used for indicating the electrical signal amplitude from the OA power meter. The OA cell was connected with a vacuum system intended for changing composition and pressure of gases. The experiments were made using a laser source or a heated wire (stretched in the middle of the cell) which imitated the heating process by absorption of laser radiation. The amplitude of the OA signal was detected as in the case of laser source used.

In the experiments special attention was paid to authenticity of our results. In all our experiments we used one and the same OAD and did not change the cell or microphone to exclude the influence of its characteristics on the form of an OA signal.

As was noted above, we studied CO_2, H_2O and their mixtures with air and N_2. The amplitude of the OA signal U was measured at the known absorption coefficient κ of a gas when the laser radiation of power W passed though the cell. The OAD sensitivity α was found from Eq. (3) when the pressure was changed.

In Fig. 1 we show a graphic representation of the measurement results of the OA signal amplitude when the pressure of the gases under study varied (here the OA signal is the ratio U/W). The obtained results can be interpreted in the same manner as it was done in Ref. 2 for the CH_4 buffer mixture:

1. Under lower pressures the OA–signal increases due to the increase of total pressure P and

2. Near the curve maxima for CO_2 the values $\omega^2 a^4/D^2\xi_1^4 \gg 1$ and $D \sim 1/P$ compensates for the signal increase due to the pressure increase.

In the calculations and discussions of the experimental data the influence of the total pressure on the microphone sensitivity was taken into account (i.e., the change of the elastic property of the membrane and ambient gas with the total pressure variation). This dependence was determined using the procedure from Ref. 3. To do this, the sinusoidal voltage with the frequency equal to the laser modulation frequency was applied to the electrode–activator. The amplitude of activating voltage was chosen so that the amplitude of the output OAD signal at a fixed pressure is the same as that produced by the absorption of laser radiation by the gas under study. For detecting the membrane oscillations we used the same scheme as in the experiments with laser radiation. The dependence of the microphone sensitivity on pressure was determined through the entire range of pressure variations for the studied gases (Fig. 2). In this figure we also give for comparison the calculational results on $S(P)$ according to Eq. (2). These results were used for determining the OAD sensitivity $\alpha' = \alpha/\varepsilon$, where ε is the microphone sensitivity according to Ref. 3.

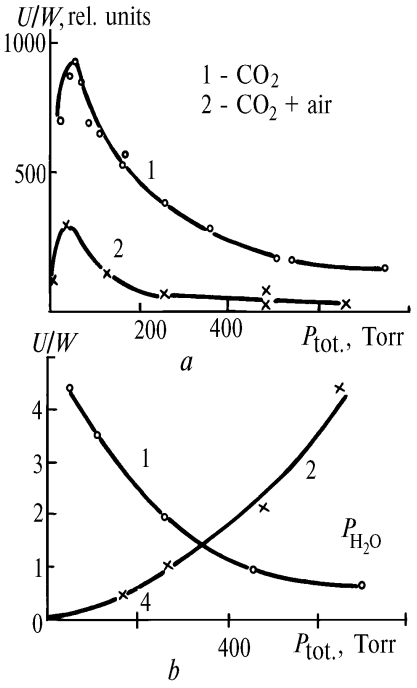

FIG. 1. A plot of the opto–acoustic signal vs gas pressure. a) 1 – pure CO_2, *2 –* CO_2 *+ air mixture,* P_{CO_2} = 3 Torr; b) *1 –* $H_2O + N_2$ *mixture,* P_{H_2O}=9.5 Torr and *2 –* H_2O *vapors.*

In Figs. 3*a* and *b* we give experimental and calculated dependences normalized by the maximum value. The calculation of $\alpha'(P)$ was made using Eq. (4) with our experimental conditions taken into account. We have made some attempts to take into account possible influence of the relaxation processes in gas, according to Ref. 3, as well as the acoustic cell properties, but no essential differences in the behavior of the dependence $\alpha'(P)$ were observed.

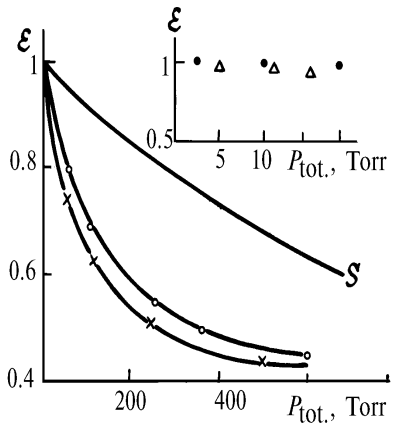

FIG. 2. The experimental dependences of the microphone sensitivity ε(*P*) *for:* Δ – H_2O, • – $H_2O + N_2$, ○ – CO_2, *and* × – CO_2 *+ air mixture in comparison with the* $S(P)$ *sensitivity.*

In Fig. 3*a* one can see essential differences in experimental data for different gases especially under high pressures (although the heat capacities of the gases involved are approximately equal). In addition, the experimental dependences $\alpha'(P)$ are affected by the type of a buffer gas. The same information can be found in Refs. 2 and 3 but the sensitivity decrease is attributed exclusively to the influence of $\kappa(P)$ and $\varepsilon(P)$. In our experiments we used the gases with different pressure behaviors of the absorption coefficients (see Fig. 4), but the signal (and sensitivity) falloff with pressure increase is observed in any case. More clearly this feature is observed for CO_2, where the absorption coefficient remains constant starting from the pressure ≈ 60 Torr. Comparison of the experimental curves $\alpha' = f(P)$ with the calculations (Figs. 3*a* and *b*) also shows that the discrepancy for H_2O can possibly be explained by a specific behavior of the H_2O absorption coefficient at low pressure in the region of CO_2–laser radiation wavelength.

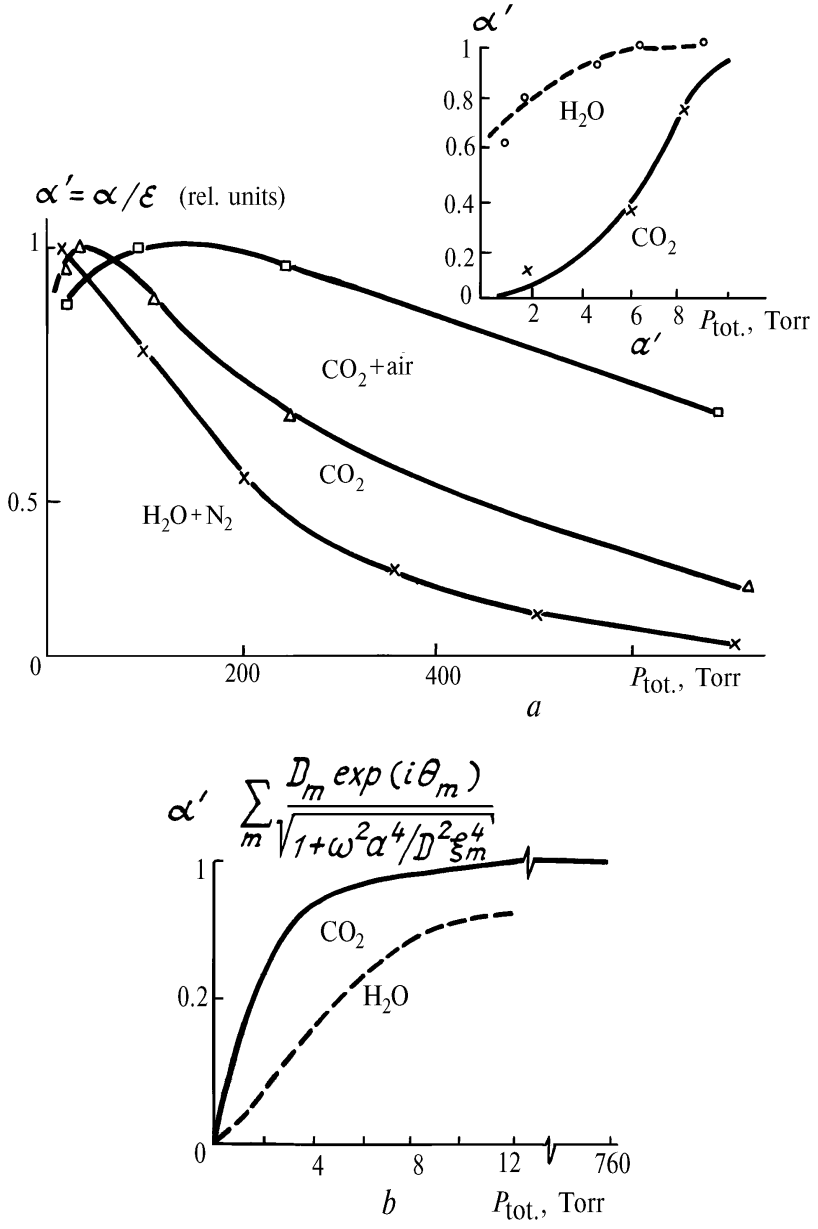

FIG. 3. The experimental (a, a') and calculated (b) dependences of the OAD sensitivity for pure gases and mixtures.

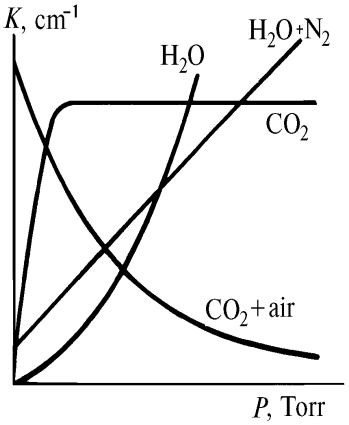

FIG. 4. Qualitative dependences $\kappa = f(P)$ *of the gases investigated for the* P(20) *line of the* CO_2 *laser.*

To elucidate the role of thermal processes in OA–signal generation a model experiment has been carried out, where the medium heating by the laser radiation was imitated by wire heating, when the half–sinusoidal voltage from an acoustic generator with $\omega = 90$ Hz was applied to it. The amplitude of heating voltage was fitted in the same manner, as for electrostatic activation so that the OAD outputs for a wire heating and heating by laser absorption were equal. To obtain the function analogous to $\alpha'(P)$ at fixed values of gas pressure, we took the ratio of the output amplitude of OAD $U(P)$ to the heating amplitude U. The change of $U(P)$ with P was taken into account according to previously determined dependence $\varepsilon(P)$. Thus obtained curves are shown in Fig. 5. It is necessary to recognize that the model situation does not always adequately explain the laser absorption process in an OA cell. Nevertheless, a decrease of the $\alpha'(P)$ with increasing pressure can be clearly seen from the obtained data.

Conclusions:

1. The OAD sensitivity decreases with the pressure increase irregardless of a gas under study what cannot be described within the available calculational models.

2. The observed falloff of the sensitivity is independent of the microphone characteristics, but can be explained by the thermal properties of the gases. We assume that when a strongly stretched membrane is used this effect is masked.

3. Interaction of gas molecules with laser radiation determines more strong dependence of $\alpha'(P)$ on the gas type than the thermal processes do.

4. The available physical representations of the relaxation processes and molecular diffusion do not allow one to adequately describe the OA–signal generation within a wide pressure range, so that a special experimental calibration for every kind of OA detector is needed.

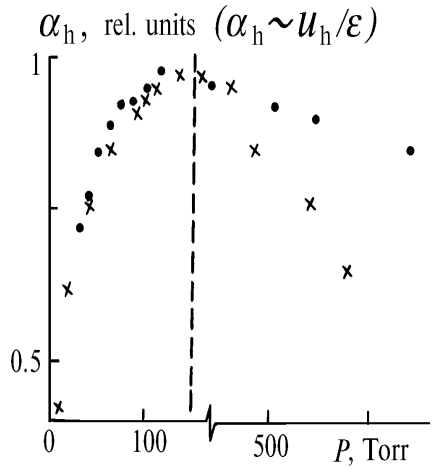

FIG. 5. The OAD sensitivity pressure dependences obtained using wire heating: × – CO_2 *and* • – CO_2 + *air mixture,* $P_{CO_2} = 3$ Torr.

To answer the question on the reasons of the discrepancies between the experimental and calculational data on the OAD sensitivity under pressures from 1 to 760 Torr the additional studies are required.

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