INVESTIGATION OF THE ABSORPTIVITY OF AEROSOL MEDIA BY AN OPTOACOUSTIC METHOD

B.G. Ageev, A.A. Zemlyanov, A.M. Kabanov, and Yu.N. Ponomarev

Institute of Atmospheric Optics
Siberian Branch of the Russian Academy of Sciences, Tomsk
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The results of experimental investigation of the absorption of IR radiation by aerosol media with an optoacoustic method are presented. The developed instrumentation is described. The absorptivity of aerosol media as a function of the radiation intensity is studied for different media. Measurements of the absorption coefficient of water aerosol in mixtures with N_2 *and* CO_2 *were carried out at the wavelength of a cw* CO_2 *laser.*

Absorption of optical radiation in the ground atmospheric layer is caused by molecular and aerosol components. In contrast to the molecular absorption, quantitative characteristics of the aerosol absorption are less studied. It is difficult to investigate systematically the aerosol absorption in its natural state. Normally indirect techniques are used to measure optical characteristics of aerosol particles, (for example, the tablet techniques,[1] i.e., pressing the aerosol particles with a filling that does not absorb radiation). Naturally, such a technique has a limited applicability especially when investigating a liquid–droplet aerosol.

The optoacoustic (OA) method[2] makes it possible to measure the amplitude of the acoustical signal (the pressure pulse) generated by the medium being filled into a closed volume, due to interaction with radiation. This amplitude is proportional to the absorption coefficient of the substance under investigation. High sensitivity of the technique makes it possible to investigate the absorption in a small volume (a few cm^3) this is especially convenient when working with gases and aerosol media, since under this condition it is easy to control and change the composition and other characteristics of the medium under investigation.

We know only a few papers, mentioned in Ref. 2 that dealt with the investigation of solid aerosol particles by the OA technique.

This paper describes the instrumentation complex designed for study of the absorption of aerosol media and presents some preliminary results of experiments carried out using this complex.

Block diagram of the measuring installation is shown in Fig. 1. The radiation sources were electroionization, pulsed, cw, and discharge gas–CO_2 lasers. Energy characteristics of the laser radiation were measured by such calorimeters as IMO–2 and optoacoustic calorimeter of our own design, and spectral composition of laser emission was measured with a panoramic spectrum analyzer.[3] The radiation was directed through the diaphragm into the cell of an OA detector containing the aerosol under investigation. The cell has a cylindric shape ($\varnothing$ = 30 mm and l = 200 mm) and is made of stainless steel. Flat windows were made of BaF_2 3 mm in thickness. The OA signal was recorded using a noncommercial plane capacitor microphone mounted into the cell wall. The microphone consists of a heavy metal electrode and the membrane made of aluminium foil. The electric signal from the microphone was the preamplified and then recorded with a storage oscilloscope. A vacuum post was used to pump out and to fill in the OA cell. The simulation of a liquid aerosol medium was performed with an aerosol generator of the "Aerosol–VI" type. Overpressure at the injector was produced not by a compressor but by the gas flow from a high–pressure cylinder. The measuring OA cell was filled either with a pure gas under investigation (N_2 or CO_2) (with the injector switched off) or with an aerosol (when switching the injector). The aerosol generator produced the particles 1–3 μm in radius. The particles of the tobacco smoke, hitting into the measuring OA cell at circulation of smoked air through were used as a solid aerosol.

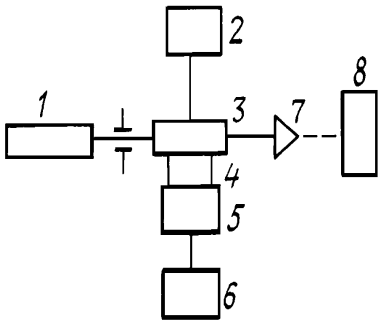

FIG. 1. Block diagram of the experimental setup: 1) CO_2*–laser, 2) System of preparation and injection of aerosol media, 3) OA cell, 4) microphone, 5) preamplifier, 6) oscilloscope, 7) calorimeter, and 8) spectrum analyzer.*

Number density of aerosol particles at the cell inlet was estimated by measuring the transmission of the medium at the 0.63 μm wavelength of a He–Ne laser and was about 10^3–10^4 cm^{-3} at the injector outlet. We failed to determine the number density of aerosol particles within the OA cell volume accurately (the error was 40–50%) and thus–estimated value of the number density was 10^2–10^3 cm^{-3}. The informative OA signal can be represented by the ratio

$$A = U/E = \alpha \cdot \kappa , \qquad (1)$$

where U is the amplitude of the electric signal at the output of the pressure sensor microphone of the OA cell, E is the power of the laser radiation measured by a calorimeter; α is the sensitivity of the OA detector, K is the absorption coefficient of the mixture under investigation.

At the first stage of the experimental study we studied some peculiarities of generation of an acoustic signal in an

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aerosol medium excited by a powerful laser pulse depending on the pulse intensity. The electroionization CO_2–laser with nonselective resonator was used as a source of exciting radiation. The spectrum of the laser radiation involved 3 or 4 components around the IP(20) line containing ~ 80% output power. The laser pulse duration was 3 μs. During the measurement process the parameter A was determined as a function of the laser radiation intensity and of a composition of the medium under investigation. The results obtained are shown in Fig. 2. When filling the OA cell with cleaned air (by bleeding through a glass filter) and measuring the value A no dependence of A on the laser radiation intensity I_l (this being increased up to 1 MW/cm^2) was revealed. In the case of water aerosol the value A increases two times but also is independent of I_l. In the case of solid aerosol particles (smoke) the value A becomes larger but nevertheless no dependence on I_l is observed at $I_l \leq 1$ MW/cm^2. It should be noted that the value $I_l \sim 1$ MW/cm^2 is below threshold values of nonlinear effects in liquid and solid aerosol particles (such as surface and volume evaporation, inflammation, and sublimation). The appearance of a particulated substance in a molecular gas absorbing the laser radiation affects the absorption when the radiation intensity is sufficient for saturation of the molecular gas absorption solely.

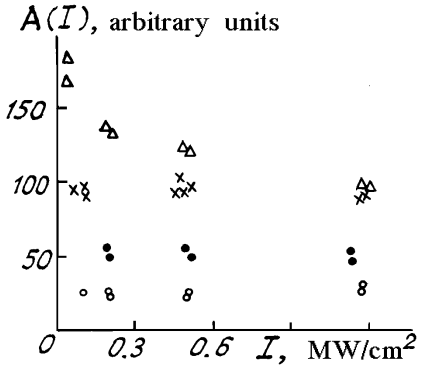

FIG. 2. Absorptivity of the medium as a function of the radiation intensity (at the total pressure of ~ 1 atm): open circles are air, close circles are air and water aerosol, crosses are air and smoke, and triangles are air and CO_2.

The effect of absorption saturation in a mixture of air with carbon dioxide irradiated by a CO_2–laser radiation is observed (see Fig. 2) already at a moderate intensity of $I_l \sim 0.2$–0.3 MW/cm^2 (see Ref. 4).

The saturation effect (nonlinear dependence of A on I_l) disappears with the appearance of aerosol particles (smoke or water droplets) with the size ~ 1 μm and number density above 10^2 cm^{-3}. Such a behavior of the absorptivity of an aerosol well agrees with the estimates done in Ref. 5, where it was shown that at a certain concentration and size of aerosol particles the heterogeneous relaxation of vibrationally excited gas molecules on the surface of particles can be more rapid than the vibrational. Appearance of an additional channel for the relaxation of vibrationally excited molecules of CO_2 leads to a decrease of the characteristic relaxation time of the population of the upper level T_1 and to an increase of the intensity value which is sufficient to reach the saturation since $I_s \sim T_1^{-1}$.

The appearance of a particulated substance in a gas medium leads to the change of the shape of the temporal behavior of the OA signal. When filling the measuring OA cell with the air cleaned using a filter, the recorded signal $U(t)$ has a typical shape (see Fig. 3*a*) caused by a superposition of the acoustic "heat" and the acoustic "sound" signals.[2,4] The presence in a gas of water droplets or smoke particles results in changes of a signal shape (Fig. 3*b*). The periodic structure observed is associated with the standing acoustic wave. The existence of such a sharp variability in the temporal behavior of the OA signal caused by aerosol particles in the volume under investigation can be used for detecting aerosols and estimating their concentration.

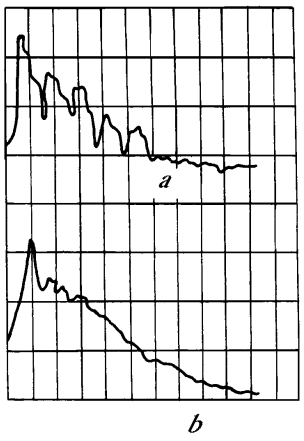

FIG. 3. Temporal behavior of the OA signal (1 division of horizontal scale is equal to 5 ms): a) pure air and b) aerosol.

The next stage of the experiment was aimed at measuring absorption coefficient of water aerosol in the mixture with N_2 and CO_2. The measurements were carried out at the wavelength 10.6 μm ($P20$ line) of a cw CO_2 laser. The radiation intensity was amplitude modulated by square pulses (τ = 5 ms and E = 25 mJ). A mechanic chopper installed outside the laser resonator was used for modulation. The measuring process involved determination of the value A successively in pure gas and aerosol. The data obtained are presented in the table (the error of determination of the value A is about 10%).

TABLE I.

Content of the OA cell (P_t = 760 Torr)	The value of A parameter (arbitrary units)	Absorption coefficient of the aerosol component k_a, cm^{-1}	Mean value k_a, cm^{-1}	Calculated value k_a, cm^{-1}
N_2	0.056	–	$9.6 \cdot 10^{-6}$	$4.4 \cdot 10^{-6}$
N_2 + aerosol	0.1	$6.9 \cdot 10^{-6}$		
CO_2	8.4	–		
CO_2 + aerosol	8.45	$11 \cdot 10^{-6}$		

For known K value in pure gases the calibration of the OA detector was carried out by Eq. (1), i.e., the value α, which was used subsequently for the case of an aerosol mixture, was determined. It was assumed that in the measurements with N_2 the OA signal was caused by the background absorption by the cell windows, and the equivalent absorption coefficient was $k_b = 8.8 \cdot 10^{-6}$ cm^{-1} (see Ref. 6). In the case of CO_2 the calculated value of the absorption coefficient k_{CO_2} (p = 760 mm Hg) = $1.8 \cdot 10^{-3}$ cm^{-1} was used. The absorption coefficient k_a of water droplet aerosol found from the measurements with N_2 at the number densities realized in the cell (~ 10^2 cm^{-3}) was about $7 \cdot 10^{-6}$cm^{-1}. The measurements with CO_2 gave $k_a \sim 11 \cdot 10^{-6}$cm^{-1}. Some difference is caused, in our opinion, by small uncontrolled admixtures, for example, H_2O in gases that also absorb the radiation. For more accurate measurements it is necessary to use chemically clear buffer gases. The calculated value k_a obtained from the data of Ref. 7 for the conditions of our experiment and the monodisperse aerosol consisting of the particles 2 μm in radius is presented in the table. Thus, we have a good agreement between calculated and empiric values of k_a. The agreement can be better if determination of the number density of aerosol particles inside the OA cell is more accurate.

The above results demonstrate the principle possibility of investigating aerosol media (containing both solid particles and liquid droplets) by the OA technique. The possibility of energy exchange between the vibrationally excited molecules and aerosol particles is indirectly confirmed.[5] Further development of quantitative measurement techniques including measurements of the energy exchange between the vibrationally excited molecules and aerosol particles needs for a number of additional experiments, including measurements of absorptivity of different gases in mixtures with weakly absorbing aerosol particles.

In should be noted that an OA setup normally used in spectroscopic studies can be used in the above–discussed investigations practically without any modifications that makes this method very convenient.

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