OPTO–ACOUSTIC DETECTION OF LOW CONCENTRATIONS OF CH_3OH, CH_3CN, AND SO_2

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The design of an opto–acoustic detector (OAD) with a Helmholtz cavity is described. Data on the OAD frequency and phase parameters measured at a pressure of 0.5 Torr *for pure* CH_3OH *for the lasing line of a* CO_2 *laser 9P(16) and the steepness of the Volt–Watt characteristic for pure* CH_3OH *and* CH_3OH *rarefied with air are presented. The limitting sensitivity and minimum detectable concentration of the spectrophone are estimated.*

The following data have been obtained: $C_{min}= 2.9\cdot10^{-6}$ *for* CH_3OH *for the lasing line of the* CO_2 *laser 9P(16), and* $C_{min}= 5.8\cdot10^{-4}$ *for* SO_2 *for the* lasing *line of the* CO_2 *laser 9R(18). Some measurements of the collisional broadening of the absorption lines of the* CH_3OH , CH_3CN , *and* SO_2 *molecules are presented. These values are (14 ± 2)*MHz/*Torr, (17 ± 3)*MHz/Torr, *and (12 ± 2)*MHz/Torr, *respectively.*

INTRODUCTION

At present the development of new techniques and facilities for monitoring the smoke emissions of industrial objects (for example, heat–and–power plants) is of practical interest. There exists a large number of methods for analyzing the composition of gaseous mixtures with the sensitivity being on a level with the maximum permissible concentrations (MPC). The standard methods, such as the chemical ones and the optical methods with a heat source of radiation, have typical drawbacks, namely, a long time of the analysis, low resolution, and insufficient reproducibility when analyzing the multicomponent gaseous mixtures.

The method, which combines an opto–acoustic detector (OAD) with a laser radiation source, possesses the necessary sensitivity. With the help of the OAD, a sensitivity on the ppb level has been demonstrated for strongly absorbing gases.[1,2]

In this paper in Ref. 3 we describe a simple and compact OAD with a Helmholtz cavity based on the analysis presented and give some results of spectral measurements for SO_2, CH_3OH, and CH_3CN. In addition, we discuss the possibility of using such detectors to determine SO_2 content in the emissions of a heat–and–power plant. In the development of the OAD we paid great attention to its reliability and decreasing its sensitivity to external vibrations and acoustic noise, what is especially important for its industrial and field applications.

EXPERIMENTAL RESULTS

The design of the developed OAD is shown in Fig. 1. A channel 15 mm in length and 6 mm in diameter with the windows made of KBr at the end faces serves as an acoustic resonator. It is connected with a cavity, in which a microphone is placed, by a channel 4 mm in diameter and 5 mm in length. In order to equalize the pressures on both sides of the diaphragm when pumping out, several holes of 1 mm in diameter were drilled in the inset of an MKE–3 commercial microphone. The signal from the microphone was amplified with a preamplifier mounted together with the OAD in a common screened housing.

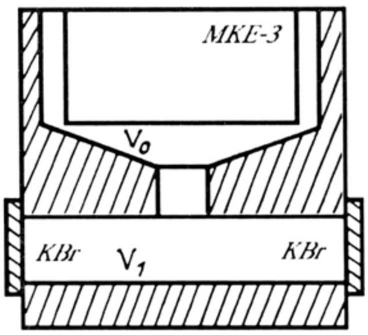

FIG. 1. The design of the detector with the Helmholtz cavity; V_0 *is the volume of the cavity and* V_1 *is the volume of the channel for the laser transmitted radiation.*

Block diagram of the experimental setup is shown in Fig. 2. In experiments the waveguide CO_2 laser[4] *1* with the diffraction grating was used for line selection. When recording of the spectra, the frequency tuning of the laser was made by varying the cavity length with the help of a piezoceramic corrector. The range of the frequency tuning of the laser was 300 MHz, the pressure of the working mixture was 70–90 Torr, and the output power of the laser beam was 1 W. The laser radiation was amplitude modulated with the help of the ML–7 electro–optical modulator *2* and then was directed to the OAD channel *3*. The modulator was controlled by the audio–frequency generator *5* and by the amplifier *4*. The degree of modulation reached 70%. The mean power of laser radiation was measured at the output of the OAD by the power meter *7* and was equal to ~ 300 mW at the line center. The OAD cell was connected with the vacuum station. When recording of the spectra the signal from the synchronous detector was applied to the *Y*–input of the automatic plotter *8*. A saw–toothed voltage from the generator *9* with a 1–10 min period was applied to the *X*–input of the automatic plotter and to the piezoceramic corrector through the high–voltage amplifier.

The resonance frequency of the OAD was estimated according to Ref. 5 and equaled 6.15 kHz. The actual resonance frequency was close in value to the calculated one (f ~6.4 kHz). The frequency and phase responce of the OAD measured at a pressure of 0.5 Torr for pure CH_3OH for the lasing line of the CO_2 laser 9P(16) are shown in Fig. 3. The steepness κ of the Volt–Watt characteristic of the OAD was 60 V·cm/W for pure CH_3OH and 63 V·cm/W when it was rarefied with air. The measured values varied insignificantly for the pressure range in which the line broadening was uniform (20–760 Torr), and for this reason it might serve as a parameter of the OAD. The noise u_n at the OAD output was 0.5 mV for the 10 s integration time of the synchronous detector. This corresponded to the limiting sensitivity of the spectrophone[6]

$$(\alpha \cdot W)_{min} = \frac{u_n}{\kappa} = 8.3 \cdot 10^{-6}\ \mathrm{W/cm},$$

where α is the absorption coefficient and W is the mean power of incident radiation.

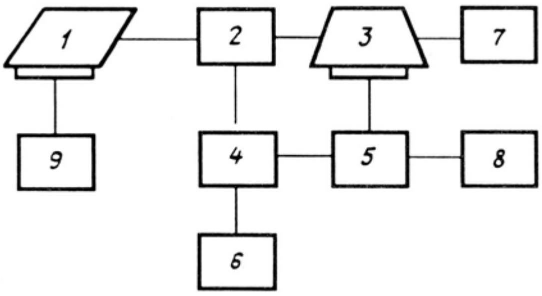

FIG. 2. Block diagram of the experimental setup (the description is given in the text).

The concentration sensitivity (minimum detectable concentration of a gas in the mixture under study) was estimated using the formula[1,6]

$$C_{min} = \frac{u_n}{\varphi \cdot \alpha_0 \cdot p \cdot W},$$

where α_0 is the absorption coefficient of the impurity at the atmospheric pressure at a given wavelength of laser radiation and p is the total pressure of the mixture.

In our case (W ~ 200 mW) for CH_3OH for the line 9P(16), α_0 equals 13.68 $cm^{-1} \cdot atm^{-1}$ (see Ref. 7), and $C_{min} = 2.9 \cdot 10^{-6}$. For SO_2 for the line 9R(18), $a_0 = 0.068$ $cm^{-1} \cdot atm^{-1}$ (Ref. 8), and $C_{min} = 5.8 \cdot 10^{-4}$.

The background signal due to absorption of radiation by the windows and walls of the cell in this case did not exceed the electric noise at the OAD output. The experimentally measured concentration sensitivity is not very high, but it can be increased up to the level of the MPC by using a more powerful CO_2 laser (~10 W) and a more sensitive microphone.

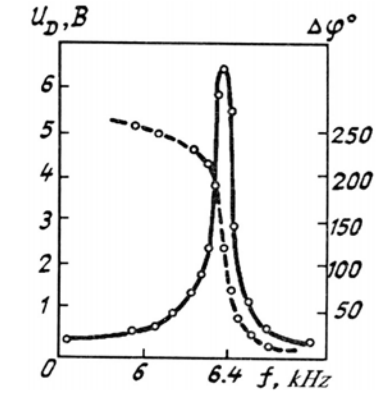

FIG. 3. The frequency (solid line) and phase (dashed line) rresponses of the OAD measured at a pressure of 0.5 Torr for pure CH_3OH *for the lasing line of the* CO_2 *laser 9P(16).* U_D *is the voltage at the detector output and* Δζ *is the phase of the opto-acoustic signal.*

In order to analyze the composition of a gaseous mixture, it is necessary to know the basic spectroscopic parameters of the gases to be examined, namely, the frequency of the centers of the absorption lines and the coefficients of collisional broadening. With the help of the OAD we have determined the widths of the absorption lines of CH_3OH, CH_3CN, and SO_2 gases at the pressure varying from 0.3 to 5 Torr. To record the absorption spectra, we have chosen lasing lines of the CO_2–laser for which the detuning from the centers of the absorption lines was minimum. The observed line shape agrees well with the shape described by the product of the Voigt profile and the function, which describes the dependence of the laser power on frequency. The measured dependences of the widths of the lines (at half–maximum of the absorption coefficient) on the pressure are shown in Figs. 4 and 5. In the case of CH_3OH and CH_3CN gases we measured self–broadening while for SO_2 – broadening by air. The initial pressure of SO_2 equaled to 0.9 Torr. The laser frequency was determined based on the voltage applied to the piezoceramic drive of the CO_2 laser. In addition, we take the nonlinearity of the piezoceramic drive characteristic was taken into account and calibrate the sensitivity according to the well–known intermode interval of the laser spectrum.

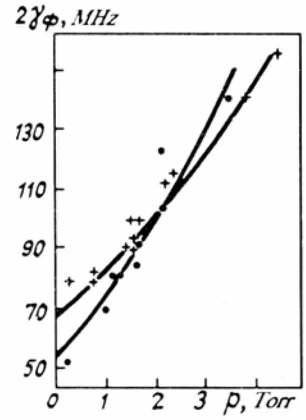

FIG. 4. The linewidth vs pressure. The crosses stand for pure CH_3OH *for the lasing line of the* CO_2 *laser 9P(24) and the dots denote the results for pure* CH_3CN *for lasing line of the* CO_2 *laser 10P(20).*

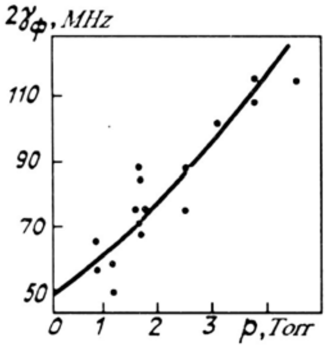

FIG. 5. The linewidth vs pressure of the mixture of SO_2 *with air. The pressure of* SO_2 *equals to* 0.9 *Torr, p is the total pressure. The lasing line of the* CO_2 *laser 9P(18) was used in this case.*

The coefficient of collisional broadening was calculated based on the experimental dependences presented in Figs. 4 and 5 with the help of the least–squares technique. When processing the results, the following formula, which relates the width of the observed shape of the absorption line $2{\cdot}\gamma_\Phi$ with its Doppler $2{\cdot}\gamma_D$ and Lorentz $2{\cdot}\gamma_L$ widths (see Ref. 1, p. 76) was used:

$$\cdot\gamma_\Phi = \gamma_D\,(0.729 + 0.526a + 0.95a^2)^{1/2}\sqrt{\ln 2}\ ,$$

where $a = \sqrt{\ln 2}{\cdot}\gamma_L/\gamma_D$, $\gamma_L = \gamma_{L0}{\cdot}p$, γ_{L0} is the coefficient of collisional broadening, and p is the gas pressure.

The following coefficients of collisional broadening γ_{L0} have been obtained: (14 ± 2) MHz/Torr for CH_3OH. (17 ± 3) MHz/Torr for CH_3CN (self–broadening), and (12 ± 2) MHz/Torr for SO_2 (the mixture of SO_2 and with air).

The accuracy of the linewidth measurements was determined by the errors in calibration of the piezoceramics and in normalization of the opto–acoustic signal by the laser power and equaled ±10 MHz. The linewidth as a function of pressure calculated from the above formula is shown in Figs. 4 and 5.

CONCLUSION

As follows from the above said, the Helmholtz cavity provides for tuning the resonance frequency in a wide range, with practically unchanged dimensions of the OAD. This can be achieved, for example, by varying the geometric size of the connecting channel. In addition, the resonance frequency can be tuned to the region in which the external acoustic noise is minimum. The OAD can be employed as a detector of the atmospheric pollutions and as a laser spectrometer. Such an OAD, being compact, simple, and noiseproof, can be used under the industrial conditions.

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