PHOTOACOUSTIC DETECTION OF XYLENES

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A feasibility to detect xylene (C_8H_{10}) *isomers in air using* $^{12}C^{16}O_2$ *laser is demonstrated. The results of photoacoustic measurements of absorption coefficient of p-xylene at* CO_2*-laser wavelengths within* 10 μm *band are presented. Optimal conditions for xylene vapor detection at a level of* 1 ppm *are determined by numerical simulation.*

INTRODUCTION

When performing a complex analysis of air pollution, it should be taken into account that now one of the main gaseous pollutants are hydrocarbons. Aromatic hydrocarbons (in particular, xylenes) are used in production of plastics, dyes, insecticides, medicines, and motor fuels. They are also contained in the exhaust gases of gasoline engines.

Photoacoustic spectroscopy is one of the promising spectroscopic methods for detection of trace gases. Among its advantages are quite simple experimental scheme, small size of the devices, as well as its high sensitivity. If tunable CO_2 lasers are used in PA gas analysis, it becomes feasible to monitor a large number of substances, important from the ecological point of view, having concentrations of the order of 10^{-9} (Ref. 1).

In this work we have determined, by numerical simulation, conditions and spectral ranges optimal for the PA detection of *p*-, *m*-, and *o*-isomers of xylene (C_8H_{10}) in air using $^{12}C^{16}O_2$ laser with their concentrations being at the level of 1 ppm. In computations we used the values of absorption coefficients of xylene isomers obtained by a photoacoustic method.[1] To check these data, we have conducted our own measurements of absorption coefficients of *p*-xylene at the lasing lines of $^{12}C^{16}O_2$.

EXPERIMENTAL RESULTS

The measurements have been done with a PA spectrometer using a $^{12}C^{16}O_2$ laser described in Ref. 2. In order to decrease the background,[3] windows of the measurement cell are made of KCl. The PA signal U at the microphone of the PA detector is defined as

$$U(\lambda) = \alpha\ W(\lambda)\ (Kx + \beta), \qquad (1)$$

where K is the absorption coefficient of the gas under analysis, x is its concentration, W is the output laser power, α is the sensitivity of a PA detector, and β is the absorption by foreign interfering gases, aerosol extinction, water vapor continuum absorption, and the like. To obtain absolute values of the absorption coefficients, the PA detector was calibrated. To this end, the measurement cell (L = 100 mm and ∅ = 15 mm) was filled with a reference mixture CO_2–N_2 (produced at the ANALITPRIBOR Production Association, Smolensk) which contains a known quantity of CO_2. During the calibration the value of U was measured at IP(20) line with varying CO_2 content in the reference mixture (at the total pressure of the mixture in the cell of 760 Torr and the temperature of 293 K). The calibration results are shown in Fig. 1. The mixture absorption coefficients were calculated based on the data from Ref. 4 with regard to the CO_2 partial pressure taking place in the experiment.

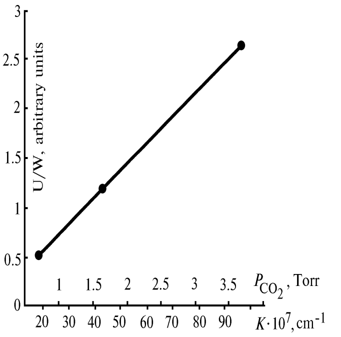

FIG. 1. The PA detector calibration plot.

The absorption coefficients of *p*-xylene of the "Ch"–class (produced at the REAKhIM Plant, Angarsk) were measured. Under study was the mixture of xylene vapors with nitrogen. To prepare the mixture, we allowed xylene vapor to bleed into an evacuated cell of the PA detector from a prepumped-out flask. Once the cell has been filled with xylene vapor up to a certain pressure, a pressure drop was observed due to interaction with walls.[1] The establishment of the equilibrium state, which is characterized by a stable pressure and a constant PA signal, took about 5 min. Then the cell was filled with nitrogen up to the pressure of 760 Torr and values of PA signals at different lasing lines were measured (the mixture temperature in measurements, as in the calibration, was 293 K). The values of the corresponding absorption

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coefficients were determined from the results of measurements and the calibration.

The data in Table I were obtained from 3–5 measurements, each being done with a new portion of xylene. For a comparison we also present the data of PA measurements from Ref. 1. As is clearly seen, the values of the *p*-xylene absorption coefficients presented coincide within the experimental error.

TABLE I. Absorption coefficients of p-xylene at the lasing lines of $^{12}C^{16}O_2$ *laser.*

Lasing line	λ, μm	K, cm^{-1} · atm^{-1}	
		Ref. 1*	Our data**
P12	10.514	0.076	0.080
P14	10.533	0.073	0.077
P16	10.552	0.072	0.076
P18	10.571	0.071	0.064
P20	10.591	0.073	0.062
P22	10.612	0.068	0.057
P24	10.632	0.065	0.057
P26	10.653	0.063	0.060
P28	10.675	0.060	0.059

* The data from Ref. 1 are recalculated for our experimental conditions. The experimental accuracy is about 5-8%.

** The experimental accuracy of our data is about 10%.

NUMERICAL SIMULATION

In this work we have paid special attention to selecting optimal spectral ranges for a CO_2-laser-based PA gas analyzer for xylene isomers. The selection was done by a comparison of the air absorption with the net absorption of xylene isomers. It was assumed in simulations that there is aerosol component in air. As follows from the above, the coefficient β entering into Eq. (1) can be presented as

$$\beta = \sum_{j=1}^{m} K_j(\lambda)\, x_j + \beta_a(\lambda) + \beta_c(\lambda), \qquad (2)$$

where x_j is the concentration of the jth interfering gas, $K_j(\lambda)$ is the absorption coefficient of the jth gas, $\beta_a(\lambda)$ is the extinction due to aerosol particles contained in air, $\beta_c(\lambda)$ is the water vapor continuum absorption.

To find the optimal spectral ranges, we proposed to consider three model situations. It was assumed in the first situation that measurements are conducted in air. In the second situation air was considered to be dried from water vapor, and in the third situation the air was assumed to be free of water vapor and carbon dioxide.

The absorption coefficients of atmospheric gases were computed in simulation using the line-by-line method based on the HITRAN data base[5] of spectral line parameters for 100 transitions of the $^{12}C^{16}O_2$ laser. The absorption coefficients of the xylene isomers were taken from Ref. 1. The concentrations of the atmospheric gases used in computations are presented in Table II. The concentration of the xylene isomers was taken 1 ppm (according to Ref. 6, MPC for xylene isomers is 50 mg/m^3 or 11 ppm).

TABLE II.

Gas	H_2O	CO_2	O_3	N_2O	CH_4
x, ppm	$1.88{\cdot}10^5$	$3.3{\cdot}10^2$	$3{\cdot}10^{-2}$	$3.2{\cdot}10^{-1}$	$1.7{\cdot}10^0$
SO_2	NO_2	NH_3	C_2H_6	C_2H_4	C_6H_6
$3{\cdot}10^{-4}$	$2.3{\cdot}10^{-5}$	$5{\cdot}10^{-4}$	$2{\cdot}10^{-2}$	$2{\cdot}10^{-2}$	$2{\cdot}10^{-2}$

Analysis of the simulation results obtained (Fig. 2) allows us to conclude that

– in natural air it is impossible to find the xylene isomers concentration at the level of 1 ppm (it becomes feasible only at the level of MPC) on either 9 μm or 10 μm range of $^{12}C^{16}O_2$ laser generation (see Figs. 2*a* and *b*);

– in the air free from water vapor it is possible to detect xylene isomers even at concentration of 1 ppm but only in the 10 μm range (see Figs. 2*c* and *d*), it corresponds to 10P(10)–10P(50) transitions of $^{12}C^{16}O_2$ laser;

– in the air free from water vapor and carbon dioxide the xylene isomers can be detected only in the 10 μm range also, the detection at the level of concentrations below 1 ppm is possible (see Figs. 2*e* and *f*) in this case as well.

CONCLUSIONS

Based on the experimental results on the absorption coefficients of *p*-xylene and the numerical simulation aimed at determination of the feasibility to detect the xylene isomers in air using the $^{12}C^{16}O_2$-laser-based PA gas analyzer, the following conclusions can be drawn:

– the absorption coefficients of *p*-xylene obtained in this work agree with the analogous data obtained in Ref. 1 within the experimental error;

– for successful detection of the xylene isomers in air the mixture under study should be free from water vapor;

– the detection is possible only in the 10 μm range of $^{12}C^{16}O_2$ laser generation;

– for a more accurate detection of the xylene isomers with their concentration below 1 ppm the air mixture under study should be free not only from water vapor but also the carbon dioxide and aerosol.

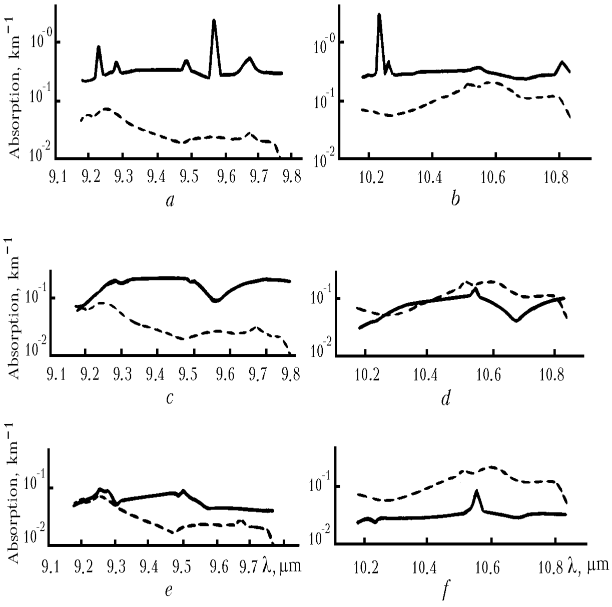

FIG. 2. The absorption coefficients of air (solid lines) and the mixture of xylene isomers (dashed lines) for the three situations: 1) natural air (a and b), 2) air free from H_2O *(c and d), and 3) air free from* H_2O *and* CO_2 *(e* and *f) for* 9 μm *(a, c, e) and* 10 μm *(b, d, f) ranges of* CO_2 *laser generation.*

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