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Spectrophone Measurements of Air Pollutants Absorption Coefficients at CO₂ Laser Wavelengths II

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SPECTROPHONE MEASUREMENTS OF AIR POLLUTANTS ABSORPTION
COEFFICIENTS AT CO₂ LASER WAVELENGTHS II

KEY WORDS: laser optoacoustic technique, absorption
coefficients, air pollutants

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Abstract

Laser optoacoustic spectroscopy technique has been used to measure the absorption coefficients of eight gas pollutants at CO₂ laser wavelengths between 9.2 μ m and 10.8 μ m. All measurements were performed with pollutant at a low pressure in the presence of 1 atm of nitrogen. For outdoor long-optical path monitoring of air pollution pair of lines (detection and reference line) have been selected.

INTRODUCTION

It is well known that the absorption coefficients of various pollutant gases are of basic importance for air pollution monitoring with differential absorption technique (see e.g. ref.1). This paper reports some new results of absorption coefficients measurements at CO₂ laser wavelength and it represents the extension of our previous work⁽²⁾.

EXPERIMENTAL APPRATUS

All details about the experimental technique and apparatus have been

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described in the preceeding paper⁽²⁾. Same apparatus has been used again for the measurement of absorption coefficients. The only alteration has been made with the pressure gauge. In our previous experiment for the measurement of low vapour pressure of pollutants, McLeod gauge has been used. In order to avoid possible errors in vapour pressure measurements this gauge has been replaced with a capacitance manometer (MKS Instruments, sensor head model no. 310 BHS-100).

RESULTS AND DISCUSSION

First, it has been carefully checked for all previously investigated substances⁽²⁾ whether new improved technique of vapour pressure measurements could improve the accuracy or correct some systematic error in absorption coefficient measurements. It was found that, in the range of vapour pressures used in our experiment⁽²⁾, there was no difference in pressure reading between McLeod and capacitance pressure gauge. Therefore, the results for absorption coefficients of ethylene, freon 12, ammonia, benzene, trichloroethylene, ethanol and toluene can be used with confidence within the limits of estimated accuracy⁽²⁾.

New experimental results for absorption coefficients at CO₂ laser wavelengths of vinyl chloride, monochloro-ethane, sulfur dioxide, methanol isopropanol, cyclohexane, ethyl acetate and acetonitrile are given together with the results of Mayer et al⁽³⁾ in Tables 1-4. The temperature of measurement was 22±2°C.

Since the calibration of the optoacoustic cell is performed with ethylene at the wavelength of CO₂ (P 14) line whose absorption coefficient is known within ±5% (see discussion in ref. 2), estimated accuracy of our data is ±9%. Here, one should point out that a very good agreement with results of Mayer et al⁽³⁾ exists (see Tables 1-4). Unfortunately similar detailed comparison could, not be performed with the other authors^(4,5) since the results were given only in a graphical forme. However maximum

TABLE 1.
ABSORPTION COEFFICIENTS $\alpha(\text{atm cm})^{-1}$ OF VARIOUS POLLUTANTS, R BRANCHES OF THE 00^01-02^00 TRANSITION

Wavelength μm	Vinyl chloride		Monochloro-ethane		Sulfur dioxide		Methanol		Isopropanol		Cyclohexane		Ethyl acetate		Acetonitrile	
	meas.	ref. 3	meas.	ref. 3	meas.	ref. 3	meas.	ref. 3	meas.	ref. 3	meas.	ref. 3	meas.	ref. 3	meas.	ref. 3
R 36	9,192	-	-	0,012	-	-	1,29	-	2,58	0,013	1,32	0,071				
34	9,201	-	-	0,014	<0,01	0,079	-	1,29	2,61	0,015	1,41	0,066				
32	9,210	0,43	-	0,013	<0,01	0,089	-	1,33	2,63	0,015	1,62	0,056				
30	9,220	0,43	0,45	0,010	<0,01	0,072	0,11	1,33	2,65	0,015	1,72	0,051				
28	9,230	0,22	0,20	0,014	<0,01	0,070	0,092	1,66	2,68	0,017	2,23	0,051				
26	9,240	0,10	0,12	0,015	<0,01	0,093	0,105	1,55	2,65	0,017	2,53	0,061				
24	9,250	0,054	<0,05	0,013	<0,01	0,070	0,090	1,87	2,62	0,015	2,84	0,071				
22	9,261	0,054	0,05	0,012	<0,01	0,068	0,072	1,65	2,65	0,012	3,04	0,071				
20	9,271	0,17	0,15	0,014	<0,01	0,087	0,088	1,78	2,77	0,010	3,04	0,101				
18	9,283	0,054	<0,05	0,012	<0,01	0,044	0,068	1,83	2,74	0,012	3,44	0,071				
16	9,294	0,051	<0,05	0,014	<0,01	0,044	0,056	1,92	2,74	0,014	3,54	0,076				
14	9,305	0,054	<0,05	0,014	<0,01	0,043	0,054	2,33	2,79	0,011	3,85	0,086				
12	9,317	0,12	0,1	0,011	<0,01	0,043	0,048	2,59	2,98	0,010	4,55	0,076				
10	9,329	0,10	0,95	0,010	<0,01	0,043	0,044	2,22	2,77	0,010	5,26	0,091				
8	9,342	1,48	1,50	0,011	<0,01	0,043	0,036	2,15	2,74	0,010	5,57	0,081				
6	9,352	1,48	-	0,011	-	-	-	2,18	2,71	0,011	6,07	0,076				

TABLE 2.
ABSORPTION COEFFICIENTS α (atm cm⁻¹) OF VARIOUS POLLUTANTS, P BRANCHES OF THE 00⁰1-02⁰0 TRANSITION

P	Wavelength [μ m]	Vinyl chloride		Monochloro-ethane		Sulfur dioxide		Methanol		Isopropanol		Cyclohexane		Ethyl acetate		Acetonitrile	
		meas.	ref. 3	meas.	ref. 3	meas.	ref. 3	meas.	ref. 3	meas.	ref. 3	meas.	ref. 3	meas.	ref. 3	meas.	ref. 3
6	9,443	0,048	<0,05	0,033	-	-	-	2,29	-	1,89	-	0,051	-	-	-	0,091	-
8	9,458	0,17	0,15	0,033	0,03	-	-	2,37	-	1,76	-	0,061	-	12,16	-	0,093	-
10	9,473	0,32	0,30	0,038	0,04	0,007	0,010	2,70	0,010	1,60	0,083	0,083	11,75	0,113	0,113	0,129	0,113
12	9,488	0,645	0,65	0,072	0,07	0,005	0,005	3,18	0,005	1,34	0,096	0,096	11,44	0,129	0,129	0,111	0,111
14	9,504	0,052	0,05	0,018	0,02	0,004	0,005	3,67	0,005	1,10	0,106	0,106	11,34	0,111	0,111	0,157	0,157
16	9,520	0,55	0,57	0,017	0,02	0,004	0,005	4,26	0,005	1,04	0,101	0,101	11,15	0,157	0,157	0,096	0,096
18	9,536	0,77	0,75	0,019	0,02	0,004	0,005	4,51	0,005	0,96	0,101	0,101	10,43	0,096	0,096	0,111	0,111
20	9,553	2,04	2,05	0,043	0,04	<0,004	<0,005	5,00	<0,005	0,86	0,081	0,081	9,32	0,111	0,111	0,099	0,099
22	9,570	1,63	1,65	0,11	0,09	<0,004	<0,005	5,19	<0,005	0,73	0,081	0,081	8,51	0,099	0,099	0,106	0,106
24	9,586	1,46	1,45	0,013	<0,01	<0,004	<0,005	5,93	<0,005	0,66	0,126	0,126	7,09	0,106	0,106	0,111	0,111
26	9,604	1,77	1,70	0,11	0,1	<0,004	<0,005	6,00	<0,005	0,56	0,134	0,134	6,08	0,111	0,111	0,122	0,122
28	9,621	1,37	1,35	0,11	0,11	<0,004	<0,005	6,67	<0,005	0,44	0,405	0,405	4,86	0,122	0,122	0,111	0,111
30	9,640	1,21	1,20	0,15	0,13	<0,004	<0,005	7,71	<0,005	0,44	0,246	0,246	4,66	0,111	0,111	0,097	0,097
32	9,658	0,87	0,85	0,057	0,06	<0,004	<0,005	8,34	<0,005	0,36	0,153	0,153	3,14	0,097	0,097	0,091	0,091
34	9,676	1,47	1,45	0,012	0,01	<0,004	0,005	8,90	0,005	0,36	0,128	0,128	2,23	0,091	0,091	0,086	0,086
36	9,695	0,64	0,65	0,012	-	-	-	10,61	-	0,32	0,122	0,122	1,72	0,086	0,086	0,091	0,091

TABLE 3.
ABSORPTION COEFFICIENTS $\alpha(\text{atm}^{-1}\text{cm}^{-1})$ OF VARIOUS POLLUTANTS, R BRANCHES OF THE $00^0_1-10^0_0$ TRANSITION

R	Wavelength μm	Vinyl chloride		Monochloro-ethane		Sulfur dioxide		Methanol		Isopro- panol		Cyclo- hexane		Ethyl acetate		Aceto- nitrile	
		meas.	ref. 3	meas.	ref. 3	meas.	ref. 3	meas.	ref. 3	meas.	ref. 3	meas.	ref. 3	meas.	ref. 3	meas.	ref. 3
36	10,147	0,77	0,75	2,34	-	<0,004	<0,005	2,98	0,56	0,021	0,152	0,061					
34	10,158	0,12	1,10	2,35	2,37	<0,004	<0,005	3,29	0,68	0,018	0,152	0,054					
32	10,170	0,73	0,75	2,32	2,30	<0,004	<0,005	2,74	0,74	0,015	0,152	0,056					
30	10,182	1,83	0,80	2,31	2,33	<0,004	<0,005	2,52	0,86	0,015	0,202	0,058					
28	10,194	1,27	1,25	2,11	2,14	<0,004	<0,005	1,74	0,98	0,015	0,202	0,053					
26	10,207	0,93	0,95	1,89	1,85	<0,004	<0,005	1,87	1,08	0,013	0,152	0,056					
24	10,220	1,62	1,60	1,59	1,57	<0,004	<0,005	1,70	1,44	0,018	0,152	0,061					
22	10,233	1,02	1,00	1,36	1,34	<0,004	<0,005	1,66	1,77	0,015	0,303	0,058					
20	10,247	1,47	1,45	0,94	0,97	<0,004	<0,005	2,03	1,95	0,011	0,202	0,056					
18	10,260	1,21	1,20	0,82	0,78	<0,004	<0,005	1,37	2,43	0,011	0,152	0,051					
16	10,274	1,02	1,00	3,34	3,34	<0,004	<0,005	1,74	2,53	0,010	0,152	0,051					
14	10,289	1,27	1,25	2,17	2,14	<0,004	<0,005	2,29	2,91	0,013	0,202	0,056					
12	10,303	1,12	1,10	1,29	1,25	<0,004	<0,005	1,48	3,02	0,020	0,202	0,056					
10	10,318	1,63	1,60	1,64	1,65	<0,004	<0,005	1,55	3,09	0,015	0,101	0,056					
8	10,334	1,03	1,05	1,69	1,67	<0,004	<0,005	1,59	3,13	0,015	0,101	0,058					
6	10,349	3,51	3,50	1,76	1,77	<0,004	<0,005	2,00	3,15	0,013	0,101	0,058					

TABLE 4.
ABSORPTION COEFFICIENTS $\kappa(\text{atm cm})^{-1}$ OF VARIOUS POLLUTANTS, P BRANCHES OF $00^0_1-10^0_0$ TRANSITION

P	Wavelength $ \mu\text{m} $	Vinyl chloride		Monochloro-ethane		Sulfod dioxide		Methanol		Izopro- panol		Cyclo- hexane		Ethyl acetate		Aceto- nitrile	
		meas.	ref. 3	meas.	ref. 3	meas.	ref. 3	meas.	ref. 3	meas.	ref. 3	meas.	ref. 3	meas.	ref. 3	meas.	ref. 3
6	10,453	1,33	1,35	1,05	1,02	0,004	0,005	1,87	3,55	0,015	0,101	0,054					
8	10,476	1,02	1,00	0,66	0,63	0,004	0,005	1,87	3,67	0,010	0,202	0,056					
10	10,494	1,35	1,35	0,45	0,41	0,004	0,005	1,83	3,78	0,018	0,304	0,056					
12	10,513	1,32	1,30	0,25	0,22	0,004	0,005	1,70	3,55	0,021	0,456	0,053					
14	10,532	1,79	1,78	0,19	0,17	0,004	0,005	1,66	3,17	0,025	0,506	0,059					
16	10,551	1,74	1,72	0,064	0,06	0,004	0,005	1,42	3,02	0,020	0,506	0,063					
18	10,571	2,06	2,05	0,062	0,06	0,004	0,005	1,18	3,02	0,020	0,709	0,063					
20	10,591	2,32	2,30	0,062	0,06	0,004	0,005	1,14	2,87	0,010	0,810	0,066					
22	10,611	8,82	8,80	0,15	0,12	0,004	0,005	1,09	2,74	0,020	0,861	0,069					
24	10,632	3,43	3,42	0,165	0,17	0,004	0,005	1,29	2,63	0,020	0,861	0,071					
26	10,653	2,52	2,50	0,172	0,17	0,004	0,005	0,81	2,51	0,020	0,963	0,099					
28	10,674	2,01	2,00	0,22	0,20	0,004	0,005	0,42	2,23	0,021	0,912	0,101					
30	10,696	2,12	2,10	0,163	0,16	0,004	0,005	0,57	1,95	0,021	1,01	0,111					
32	10,718	1,52	1,50	0,20	0,18	0,004	0,005	0,66	1,62	0,021	1,11	0,122					
34	10,741	1,89	1,90	0,21	0,19	0,004	0,005	0,64	1,44	0,023	1,11	0,111					
36	10,763	3,13	3,15	0,21	-	0,004	0,005	0,81	1,07	0,025	-	0,117					
38	10,787	1,77	1,75	-	-	-	-	-	-	-	-	-					

TABLE 5.
SUGGESTED WAVELENGTHS FOR AIR POLLUTION MONITORING

G A S	M e a s u r e			R e f e r e n c e		
	Line	wavelength μm	α $\text{atm}^{-1}\text{cm}^{-1}$	Line	wavelength μm	α $\text{atm}^{-1}\text{cm}^{-1}$
Vinyl chloride	P 22	10,612	8,82	R 18	9,282	0,054
	R 16	10,275	3,34	P 20	10,591	0,062
Monochloro-ethane	R 26	9,240	0,093	P 18	9,536	0,004
Sulfur dioxide	P 36	9,695	10,61	P 28	10,674	0,42
Methanol	P 10	10,494	3,78	P 36	9,695	0,32
Izopropanol	P 28	9,621	0,405	R 12	9,317	0,010
Cyclohexane	P 8	9,458	12,16	R 10	10,318	0,101
Ethyl acetate	P 16	9,520	0,157	R 28	10,194	0,053
Acetonitrile						

values and wavelength dependence of absorption coefficients are in good agreement with these authors^(4,5) as well.

Finally on the basis of our and other experimental results⁽³⁻⁵⁾ in Table 5 we have selected pairs of lines (detection and reference line) which should be used for outdoor long-optical path air pollution monitoring.

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