Investigation of CO_2 absorption spectra in 1 μm region under high excitation

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The absorption spectra of CO_2 have been studied within 1 μm region with the spectral resolution of 0.02 cm^{-1} under thermal excitation of molecules at temperatures from 300 to 1350 K and excitation by an electric discharge. A highly sensitive intracavity laser spectrometer based on neodimium-dopted glass laser was used in the experiment. New vibrational-rotational bands due to transitions from the (01101) highly excited vibrational state have been recorded. Spectroscopic constants for high vibrational states of CO_2 have been determined.

Carbon dioxide is one of the main gaseous constituents of the Earth's atmosphere and atmospheres of the other planets of the solar system. Investigations of its absorption spectra are needed in many problems of atmospheric optics.[1]

The IR spectra of carbon dioxide are well studied, its rotational constants have been determined for many bands, along with the intensities of individual vibrational-rotational lines as well as the integral intensities of its bands (Refs. 2 and 3). The values of rotational and centrifugal constants as well as line centers and intensities in 470–9600 cm^{-1} region can be found in the bank of spectroscopic parameters[2] for a series of CO_2 isotopes like $^{12}C^{16}O_2$, $^{13}C^{16}O_2$, $^{12}C^{18}O_2$, $^{16}O^{12}C^{18}O$, and $^{16}O^{12}C^{17}O$. The force field of the CO_2 molecule has been determined[4] thus allowing one to reconstruct with high accuracy the energy structure of CO_2 and its isotopes up to the energies of 8000 cm^{-1}.

The highest excited vibrational states of CO_2 in the atmosphere of Venus were studied with the help of a Fourier-spectrometer. The large optical depth of CO_2 there gave a possibility to record its weak absorption bands up to 10000 cm^{-1} frequency and to analyze their rotational parameters.[5]

Currently the measurements of CO_2 spectra have been being conducted with the intracavity spectrometers.[6,7] High sensitivity of these instruments allowed one to detect lines of well known bands involving those due to transitions from states with rotational quantum numbers J higher than those studied in Ref. 5. The following bands were recorded: (21132) ← (01101) ($\nu_0 = 9478$ cm^{-1}) and (11131) ← ← (01101) ($\nu_0 = 8135$ cm^{-1}) of the isotope $^{12}q\,^{16}n_2$, (20031) ← (00001), (20032) ← (00001) of $^{13}q\,^{16}n_2$, the bands (20031) ← (00001), (20032) ← (00001), (20033) ← ← (00001) of $^{12}q\,^{18}n_2$, as well as the band (20032) ← ← (00001) of $^{12}q\,^{16}n\,^{18}n$.

In this paper, we present the study of the absorption spectra of carbon dioxide in the region 9370–9470 cm^{-1} at high temperatures. We have used a highly sensitive intracavity neodimium-dopted glass laser-based spectrometer described in detail in Refs. 8 and 9.

The recording of the radiation spectra was made using a diffraction grating spectrograph DFS–8 equipped with an objective of 2500 cm focal length F. The grating of 600 grooves/mm, used in the spectrograph, was operated in the third order of diffraction at ~ 72° angle. A linear array of photodiodes comprising 1024 elements was set at the spectrograph output. Spectral resolution of the spectrograph was 0.02 cm^{-1}, the threshold sensitivity to the absorption at the emission pulse duration of ~ 1 ms was 10^{-7}–10^{-8} cm^{-1}. The CO_2 line centers were measured with the error less than 0.01 cm^{-1} relative to line centers of H_2O of the atmospheric air, that filled in the open spaces of the laser cavity.

Owing to its high sensitivity attainable due to the use of small-size cells, the intracavity spectrograph allows one to study the molecules during their external excitation leading to population of the upper vibrational states.

Thermal excitation

The simplest way to populate the energy levels with high values of J and V is heating of molecules to high temperatures. The population of the rotational level N_{VJ} with the energy E_J at thermodynamic equilibrium is determined by the Boltzmann law

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$$N_{VJ} = q_{VJ}\, N_J = (1/Q_R)\, N_V\, q_J \exp(-E_J/kT),$$

where q_{VJ} is fraction of molecules being in the vibrational state V at the level J; N_V is the population of vibrational state with the quantum number V; q_J is the statistical weight of the corresponding rotational level; $Q_R = \sum\limits_J q_J \exp(-E_J/kT)$ is the rotational partition function; k is the Boltzmann constant.

Population of a vibrational state with the energy E_V is determined by the expression

$$N_V = (1/Q_V)\, N_0\, q_V \exp(-E_V/kT),$$

where q_V and Q_V are the vibrational statistical weight and vibrational partition function, respectively.

For q n 2 $Q_R \sim T/1.12$, and $Q_V = \sum\limits_{V_1} \sum\limits_{V_2} \sum\limits_{V_3} q_V \times$ $\times \exp(-hc\nu_V)/kT$.

The temperature increase results in a redistribution of population among the energy levels, i.e., leads to an increase in the population of higher states.

For CO_2, the total partition function $Q_{VR} = Q_V Q_R$ increases from 291 at $T = 300$ K to 2164 at $T = 900$ K, what results in a change of population of the vibrational and rotational states. If the ratio of population of vibrational states (00001), (01101), (10001), and (00011) with $E_V = 0$, 667, 1345, and 2367 cm^{-1} at $T = 300$ K is 0.95:0.04:0.001:0.00006, then at $T = 1350$ K it changes to 0.20:0.10:0.045:0.023, what opens up opportunities to detect the transitions from the excited vibrational states.

As a result of analysis of the spectra, tens of new lines due to transitions from levels with large values of the rotational quantum number ($J > 80$) have been identified. Thus the “hotB band (21132)–(01101) was recorded and identified. It is a specific feature of the high-temperature spectra that high density of spectral lines is observed due to overlapping of the bands formed due to transitions from the ground and excited vibrational states.

Excitation in an electric discharge

Further increase of the temperature results in a complication of the recorded spectra, so the identification and interpretation of high-temperature bands becomes too problematic. Therefore, local resonance excitation of individual vibrational energy levels seems to be more interesting, because in this case the transitions from the CO_2 higher vibrational states can be recorded. In achieving this task, a study of absorption spectra of laser high-pressure gas-discharge tube of a CO_2 laser is quite promising. Solution of this problem can find applications to diagnostics of the CO_2-plasma, study of physics of the gas-discharge plasma in CO_2, and spectroscopy.

The discharge chamber (a CO_2 laser, assembled on the basis of universal laser system “FotonB^{10}) was installed inside a laser cavity. The cavity forming mirrors were removed and replaced by quartz windows set at the angle of ~ 5°. The length of the discharge chamber was ~ 60 cm and the discharge gap was ~ 15 mm wide. The cross section of the laser chamber is shown in Fig. 1. Inside a stainless steel tube *1*, a dielectric tube *2* with a storage capacitor C_0 and a controllable spark gap were mounted together with the peaking capacitors *3*, dielectric plate *4*, discharge gaps for preionization *5*, discharge gap *6*, and feeding metal plates with bushing insulators *7* and the holes *8* in the bottom plate.

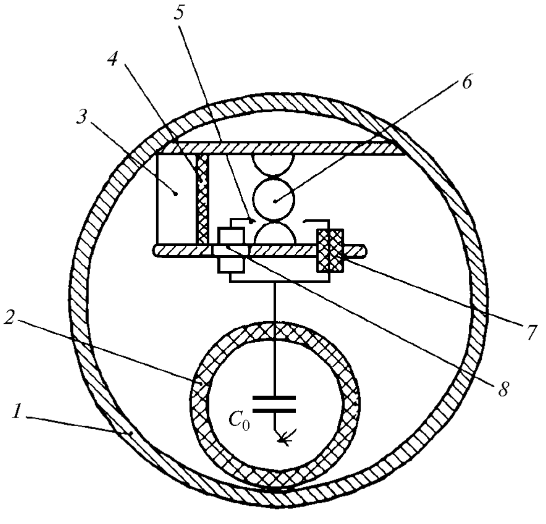

Fig. 1. Cross section of the discharge chamber used.

To obtain maximum efficiency of the discharge, the gas should get the main portion of energy at a minimum possible magnitude of the ratio E/P (E is the electric field strength and P is the pressure of working mixture). Therefore, the capacity of the reservoir capacitor ($C_0 = 10$ nF) in this circuit was chosen substantially larger than that of the peaking capacitor ($C = 0.6$ nF). This allowed us to gain the voltage pulse amplitude at the peaking capacitor and discharge gap (before its break-down) twice as large as the charging voltage U_0 of the capacitor C_0 and to deposit the main portion of energy at the voltage twice as lower as U_0. The doubling of the charging voltage facilitated the volume discharge formation, so the main contribution of energy came at a relatively low E/P. All this helped us to gain efficient generation relative to the energy stored in C_0, i.e., of the order of 10% at the emission energy of 0.65 J.

Let us point to the peculiarity revealed at recording the absorption. We failed to conduct our measurements when operating at charging voltages corresponding to CO_2 laser maximum emission for the given mixture ($U_0 \sim 20$ kV), obviously, because of the strong absorption. Lowering the charging voltage to 15 kV resulted in almost twofold decrease in the input specific energy. Only in this case we have managed to make measurements, the results of which are presented below. The intensity of the discharge glow decreased as the charging voltage decreased and the color of the discharge also changed (visually, the reddish hue in the excitation region at U_0 ~ 20 kV became blue at U_0 ~ 15 kV). Further decrease of the charging voltage as well as its increase to the magnitude higher than the optimum one resulted in the discharge contraction. The absorption in such mixtures at a comparatively large energy deposition, in pumping by the discharge initiated by an electron beam, has been recorded earlier. Thus, for example, in Ref. 11 there was recorded a multipeak mode of generation due to absorption at the pressure of the working mixture equal to 1 atm.

The system of the absorption spectra recording allowed us to conduct measurements at various moments starting from the discharge initiation. The system of control over the laser gas-discharge tube afforded a possibility to vary the characteristics of the induced discharge within wide limits both over the intensity (20–80 kV/(cm·atm)) and duration (5–80 ms). The synchronization circuit helped us to choose the optimum correlation between the starts of the laser generation and the discharge. All that in combination with the spectrometer spectral memory at the laser pulse duration from 0.2 to 2 ms enabled us to detect with a sufficient sensitivity a lot of new lines (more than 200) due to transitions from the CO_2 ground and first excited vibrational states (see Table 1).

The obtained absorption spectrum essentially differs from the CO_2 absorption spectrum at high temperature; the observed absorption lines are therewith comparable by the absorption coefficient with those within the band (20032)–(00001) (Fig. 2).

Table 1. Line centers of CO_2 bands, cm^{-1}

J	$^{12}C^{16}O_2$				*J*	$^{12}C^{16}O_2$			
	20032 − 00001	20033 − 00001		21132 − 01101		20032 − 00001	20033 − 00001		21132 − 01101
	P	*P*	*R*	*P*		*P*	*P*	*R*	*P*
0	–	–	9389.777	–	38	–	9348.310	9407.050	9435.713
2	–	9387.415	9391.260	–	39	–	–	–	9433.533
4	–	9385.775	9392.661	–	40	–	9345.510	9407.301	9432.750
6	–	9384.073	9394.022	–	41	–	–	–	9430.488
8	–	9382.313	9395.317	–	42	–	9342.610	9407.497	9429.741
10	–	9380.486	9396.547	–	43	–	–	–	9427.391
12	–	9378.587	9397.713	–	44	–	9339.740	9407.636	9426.659
14	–	9376.639	9398.821	–	45	–	–	–	9424.193
16	–	9374.624	9399.860	–	46	–	9336.680	–	9423.480
18	–	9372.547	9400.837	–	47	–	–	–	9421.004
19	–	–	–	9459.937	48	9457.609	–	–	9420.254
20	–	9370.400	9401.748	9459.027	49	–	–	–	9417.748
21	–	–	–	9457.609	50	9454.141	–	–	9417.010
22	–	9368.180	9402.596	9456.731	51	–	–	–	9414.457
23	–	–	–	9455.254	52	9450.631	–	–	9413.643
24	–	9365.930	9403.381	9454.351	53	–	–	–	9411.127
25	–	–	–	9452.781	54	9447.050	–	–	9410.287
26	–	9363.610	9404.101	9451.931	56	9443.358	–	9406.942	9406.745
27	–	–	–	9450.247	58	9439.609	–	9406.599	9403.116
28	–	9361.140	9404.757	9449.375	60	9435.780	–	9406.165	9399.489
29	–	–	–	9447.647	62	9431.860	–	9405.683	9395.793
30	–	9358.730	9405.340	9446.793	64	9427.899	–	9405.103	–
31	–	–	–	9444.965	66	9423.832	–	9404.473	–
32	–	9356.220	9405.871	9444.131	68	9419.665	–	9403.758	–
33	–	–	–	9442.222	70	9415.430	–	9402.968	–
34	–	9353.650	9406.325	9441.393	72	9411.127	–	9402.118	–
35	–	–	–	9439.394	74	9406.745	–	9401.135	–
36	–	9351.040	9406.739	9438.575	76	9402.327	–	–	–
37	–	–	–	9436.509					

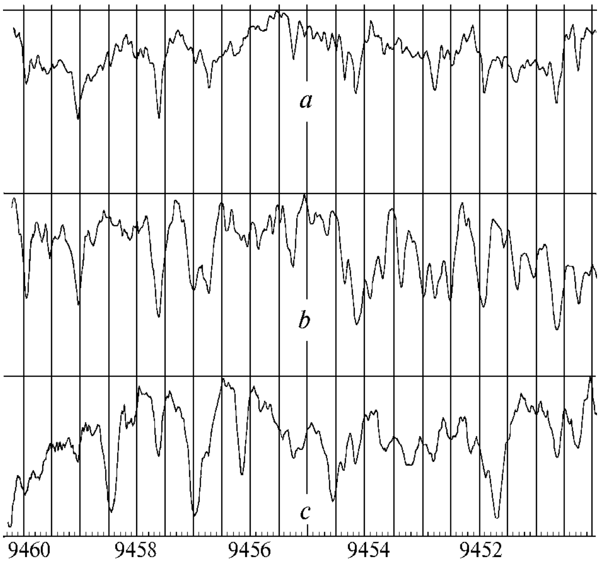

Fig. 2. CO_2 absorption spectrum in 1 μm region recorded at temperatures of 300 K (*a*), 1300 K (*b*), and in the electric discharge (*c*).

Analysis of the recorded lines

The recorded transitions from the CO_2 ground vibrational state are the transitions of Σ–Σ type, and the bands (11131) ← (01101) and (21132) ← (01101) are the transitions of o –o type, i.e., all the bands are parallel, and only *P*- and *R*-branches are observed in them. The lines of these branches are described by the following expressions:

$$P(J) = \nu_0 + B'\,(J-1)\,J - B''\,(J+1)\,J - D'\,(J-1)^2 J^2 + D''\,(J+1)^2 J^2;$$

$$R(J) = \nu_0 + B'\,(J+1)\,(J+2) - B''\,J\,(J+1) - D'\,(J+1)^2\,(J+2)^2 + D''\,J^2\,(J+1)^2,$$

where ν_0 is the band center; J is the rotational quantum number; B'', D'', B', and D' are the rotational constants of the lower and upper vibrational states, respectively.

In the class of molecules of $D_{\infty h}$ symmetry, to which the symmetric isotopes of CO_2 belong, the rotational levels are by turns symmetrical and antisymmetrical and have different statistical weights, i.e., an alternation of line intensities within the bands is observed. For CO_2, the statistical weight of symmetric levels is 1 and that of antisymmetrical levels is 0, therefore the lines with odd quantum numbers J are absent in the Σ–Σ type bands.

In transitions of Π–Π type, to which the band (21132) ← (01101) belongs, the lines with even and odd J belong to different components of *l*-duplication (c and d). They are described by rotational constants b^c, D^c, B^d, and D^d, respectively. The rotational constants of the CO_2 lower vibrational states are available in literature with high accuracy. Table 2 presents the spectroscopic constants of the recorded bands and their confidence intervals obtained by the least squares method.

Table 2. Spectroscopic constants for CO_2, cm^{-1}

State	ν_0	B	$D \cdot 10^{-7}$
20032	9516.85 (5)	0.38056 (3)	1.47 (4)
20033	9389.003 (3)	0.382361 (3)	1.752 (6)
21132 c	10145.49 (2)	0.38154 (3)	1.05 (6)
21132 d	10145.55 (3)	0.38143 (5)	−4 (2)

Note. The figures in brackets denote the value of the confidence intervals expressed in the last digit, for example, 9516.85(5) means 9516.85 ± 0000.05.

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